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RESEARCH PAPER RP1584

Part of Journal of Research of the National Bureau of Standards, Volume 32, May 1944

METHOD FOR DETERMINING INDIVIDUAL HYDROCARBONS IN MIXTURES OF HYDROCARBONS BY MEASUREMENT OF FREEZING POINTS[1,2]

By Anton J. Streiff[3] and Frederick D. Rossini

ABSTRACT

A method is described for determining individual hydrocarbons in mixtures of hydrocarbons by the measurement of freezing points. Experimental data are given for the determination of the four C_8 aromatic hydrocarbons. The uncertainty of the determination of each hydrocarbon is near ± 1 percent of the total sample.

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I. INTRODUCTION

This paper describes a general method for determining individual hydrocarbons in mixtures of hydrocarbons by measurement of freezing points. The method is based on the fact that the amount of a hydrocarbon H in an unknown mixture of hydrocarbons can be determined by measurement of the lowering of the freezing point of a sample of pure H caused by the addition to it of a given amount of the unknown mixture. If the unknown mixture contains none of the hydrocarbon H, the lowering of the freezing point will have its greatest value, which will be substantially that called for by the ideal or dilute solution laws; whereas, if the unknown is composed entirely of the hydrocarbon H, the lowering of the freezing point will be zero.

In the exact application of the method, it is important to show that the solution of the hydrocarbon H with the unknown is, within the desired limits, ideal or sufficiently dilute, so that the ideal law of the lowering of the freezing point may be applied. If the solution of the hydrocarbon H with the unknown is not ideal or sufficiently dilute, it will be necessary to separate the unknown mixture beforehand by

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Presented before the Division of Petroleum Chemistry of the American Chemical Society at Cleveland, Ohio, April 5, 1944.

[3] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

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an appropriate fractionating process into two or more portions, each of which will form substantially ideal, or sufficiently dilute, solutions with the appropriate pure hydrocarbons.

II PREPARATION OF THE SAMPLE

In order to utilize the freezing point observations in the desired manner, it is important that each mixture of hydrocarbons examined be one that forms an ideal or sufficiently dilute solution with each of the hydrocarbons to be determined. In general, this requires that the unknown mixture of hydrocarbons be composed preponderantly of hydrocarbons of a similar or nearly similar type, as for example, (a) a mixture of paraffins plus cycloparaffins or of either of these separately, or (b) a mixture of olefins, or (c) a mixture of aromatics. Such mixtures will in general be ones most likely to follow, within the desired limits, the ideal law of the lowering of the freezing point. On the other hand, mixtures containing hydrocarbons of different type (considering for this purpose paraffins and cycloparaffins to be of similar type) may be expected to show significant departures from the behavior of an ideal solution. Such mixtures would require appropriate fractionation by type before proceeding with measurements of the lowering of the freezing point.

The method of analysis described in this paper places no restriction or limitation on the boiling range of the material to be examined, although obviously the precision is likely to be better for a narrow-boiling fraction than for a very wide-boiling fraction, such as the entire gasoline fraction.

The amount of hydrocarbon material required is, for each determination, about 40 ml of the "pure" hydrocarbon and 2 to 3 ml of the unknown.

III. METHOD

Given an unknown mixture of hydrocarbons of similar type, it is required to determine the amount of a given hydrocarbon H which is in the unknown mixture. Measurement is made of the freezing point of a sample of "pure" H, and also the freezing point of a dilute solution of the unknown mixture in "pure" H. The molecular weight of the unknown is determined, if necessary, by measuring the lowering of the freezing point of another hydrocarbon, of the same type as the unknown mixture but which is not a component of the unknown mixture, on the addition to this other hydrocarbon of a measured small amount of the unknown. Let

N^p = the mole fraction of the hydrocarbon H in the given lot of "pure" H. (This will be slightly less than unity, in general.)

N^s = the mole fraction of the hydrocarbon H in the solution made by adding a small amount of the unknown to "pure" H.

N^u = the mole fraction of the hydrocarbon H in the unknown mixture.

m^p = the mass of the sample of "pure" H used in making the solution of "pure" H and the unknown.

m^u = the mass of the unknown used in making the solution of "pure" H and the unknown.

M^p = the molecular weight of "pure" H, taken to be that given by the molecular formula of hydrocarbon H.

M^u = the molecular weight of the unknown, determined, if necessary, from a lowering of the freezing point as mentioned above.

t_{f_0} = the freezing point of hydrocarbon H for zero impurity, in degrees centigrade.

t_f^p = the freezing point of the given lot of "pure" H, which, in general, will be slightly lower than t_{f_0}.

t_f^s = the freezing point of the solution of "pure" H with the unknown.

It follows that

$$N^p\frac{m^p}{M^p}+N^u\frac{m^u}{M^u}=N^s\left(\frac{m^p}{M^p}+\frac{m^u}{M^u}\right), \tag{1}$$

which is equivalent to

$$N^u=N^s-\left(\frac{m^p}{m^u}\right)\left(\frac{M^u}{M^p}\right)(N^p-N^s). \tag{2}$$

The values of N^p and N^s are given by the following relations [1, 2, 3]:

$$-\ln N^p=A(t_{f_0}-t_f^p)[1+B(t_{f_0}-t_f^p)] \tag{3}$$

$$-\ln N^s=A(t_{f_0}-t_f^s)[1+B(t_{f_0}-t_f^s)], \tag{4}$$

where

$$A=\Delta H_{f_0}/RT_{f_0}^2, \tag{5}$$

$$B=1/T_{f_0}-\Delta C_{p_0}/2\Delta H_{f_0}, \tag{6}$$

T_{f_0} = the freezing point in degrees Kelvin of pure H with zero impurity,

R = the gas constant per mole,

ΔH_{f_0} = the heat of fusion of pure H at T_{f_0},

ΔC_{p_0} = the heat capacity of pure H in the liquid state less the heat capacity of pure H in the solid state, at T_{f_0}.

In eq 2, which gives explicitly the value of the desired quantity N^u, the values of N^p and N^s are computed from eq 3 and 4, respectively, using the measured values of t_f^p and t_f^s, with the given value of t_{f_0}. It should be noted that for high precision the difference between t_f^p and t_f^s must be as precise as possible, whereas the value selected for t_{f_0} is of secondary importance, since it is used primarily as a reference point. In fact, if the sample H is sufficiently pure with N^p very nearly equal to unity, then eq 2, 3, and 4 may be simplified without significant error by substituting 1 for N^p and t_f^p for t_{f_0}, as follows:

$$N^u=N^s-\left(\frac{m^p}{m^u}\right)\left(\frac{M^u}{M^p}\right)(1-N^s) \tag{2a}$$

$$-\ln N^p=0;\ N^p=1 \tag{3a}$$

$$-\ln N^s=A(t_f^p-t_f^s)[1+B(t_f^p-t_f^s)]. \tag{4a}$$

In eq 2 (and 2a), the masses m^p and m^u are obtained from weighings on a balance, the molecular weight M^p is taken as known and equal to that of the hydrocarbon H, and the molecular weight of the unknown mixture, M^u, is determined as follows:

Given a hydrocarbon G which is not a component of the unknown mixture but which forms with it a substantially ideal or sufficiently dilute solution. Measurement is made of the freezing point of a lot of "pure" G, which should contain not more than 0.005 mole fraction of impurity, and of the freezing point of a dilute solution of the unknown in G. Let

t_f^p = the freezing point of the lot of "pure" G,
t_f' = the freezing point of a dilute solution of the unknown in G,
m^p = the mass of "pure" G in the solution,
m^u = the mass of the unknown in the solution,
M^p = the molecular weight of G, taken as known from its molecular formula,
M^u = the molecular weight of the unknown mixture.

If the freezing point of "pure" G, t_f^p, is not too much below the freezing point of G for zero impurity, t_{f_0}, then the molecular weight of the unknown is obtained with sufficient accuracy from the following equations:

$$-\ln N^p = A(t_f^p - t_f')[1 + B(t_f^p - t_f')] \tag{7}$$

and

$$M^u = M^p(m^u/m^p)N^p/(1-N^p). \tag{8}$$

In eq 7, the constants A and B are the same as before, except that they now apply to pure hydrocarbon G.

The possible precision of the method in the case of the four C_8 aromatics is as follows. It is necessary to determine the difference between t_f^p and t_f' within 0.01° C, if the amount of the given compound is to be determined to within 0.005 mole fraction, when the relative amounts of the "pure" hydrocarbon and the unknown are selected so as to give a lowering of about 2° C when none of the given compound is present in the unknown.

IV. EXPERIMENTAL PROCEDURE AND RESULTS

The use of this method is here illustrated by application to the four C_8 aromatic hydrocarbons. Since it has been shown [8, 9][4] that the four C_8 aromatic hydrocarbons follow the ideal solution laws as regards the liquid-solid equilibrium, it appeared desirable, for this system, to use as known test mixtures simply the four pure components in turn, determining in each case a component different from the one being examined so that the known would contain none of the component being determined. In these experiments, the lowering of the freezing point would, for the given molal ratios used, be a maximum, and departures from the theoretical values would be more easily recognized.

In the experimental part of the work, the determination of freezing points was made with the apparatus and procedure described in reference [3], with the following additions to the procedure:

[4] Figures in brackets indicate the literature references at the end of this paper.

(a) For best results in the case of solutions, it was found necessary to extend the observations on the equilibrium portion of the time-temperature freezing or melting curve to cover the largest possible fraction of the material crystallized or melted.

(*b*) Instead of a visual extension of the equilibrum portion of the curve to "zero" time on freezing (the time at which crystallization would have begun in the absence of undercooling), or to the corresponding time on melting, the geometrical method described in a recent report of the API Research Project 44 at this Bureau was used [4].

For certain hydrocarbons, it is found that the time-temperature freezing curve obtained in the manner referred to has no portion recognizable as representing thermodynamic equilibrium between solid and liquid. In such cases, the time-temperature melting curve is used.

To test the over-all accuracy of the method, determinations were made of the amount of ethylbenzene, of *p*-xylene, and of *m*-xylene in "pure" *o*-xylene (0.9940 mole fraction pure), and the amount of *o*-xylene in "pure" *p*-xylene (0.9948 mole fraction pure). The amounts determined (see table 1) were, respectively, 0.0090, −0.0012, 0.0138, and 0.0034 mole fraction, which values are to be compared with zero as the theoretical value.

A convenient way of tabulating the experimental results and calculations is illustrated in table 1, where the columns give, in order, the following quantities wherever appropriate (see footnotes to the table for further explanation): the freezing point for zero impurity, $N_2=0$; the resistance in ohms of the given platinum resistance thermometer at the given freezing point; the difference in resistance of the platinum resistance thermometer at the given freezing point and at the freezing point for zero impurity; the change in resistance with temperature for the given thermometer at the given mean temperature; the value of $t_{f_0}-t_f$, obtained as the quotient $(R_{f_0}-R_f)/(dR/dt)$; the value of A as defined by eq 5; the value of B as defined by eq 6; the ratio of the masses of the "pure" substance and the unknown; the ratio of the molecular weights of the unknown and the "pure" substance; and the mole fraction of the given hydrocarbon in the "pure" substance, in the solution, and in the unknown. Table 1 also gives the values of A and B, as defined by eq 5 and 6, respectively, for benzene.

For these small differences, the calculation of the value of the lowering of the freezing point may be made most conveniently and precisely by taking the difference in the two values of the resistance, R, of the resistance thermometer, and dividing by the value of dR/dt for the mean temperature. (If a thermoelement is used, the difference in the two values of the emf, E, is divided by the appropriate value of dE/dt.) For a platinum resistance thermometer for which the constants R_0, δ, β, and c $(=(R_{100}-R_0)/R_0)$ are given,

$$dR/dt=R_0c[(1+0.01\delta)-(2\times10^{-4})\delta t-(4\beta\times10^{-8})(t-75)t^2].$$

The foregoing equation is applicable for temperatures below 0° C. For temperatures above 0° C, the equation is simplified to

$$dR/dt=R_0c[(1+0.01\delta)-(2\times10^{-4})\delta t].$$

With these equations, values of dR/dt for unit values of t covering the range of interest may be tabulated and linear interpolation used for obtaining values for intermediate temperatures.

Application of the method has also been made [9] to the determination of the amounts of each of the four C_8 aromatic hydrocarbons in five different unknown mixtures consisting of C_7, C_8, and C_9 aromatic hydrocarbons, and the amounts of ethylbenzene and *p*-xylene in seven other different unknown mixtures consisting of C_7, C_8, and C_9 aromatics. For each of the first five of these unknowns, the following independent data were available to serve for comparison with the results obtained by the method of measuring freezing points:

(a) From analytical distillation data the relative amounts of the C_7, C_8, and C_9 aromatics (from which values the mean molecular weights could be calculated, as well as the percentage of the sum of the four C_8 aromatics).

(b) From analytical distillation data, the percentage of *o*-xylene in each of the unknowns.

The results obtained on one of the unknowns by the present method are given in table 1.

TABLE 1.—*Experimental data on the determination of the four C_8 aromatics in an unknown mixture of aromatics*

Material	t_{f_0}	R_f	$R_{f_0}-R_f$	dR/dt	$t_{f_0}-t_f$
ETHYLBENZENE					
	°C	*Ohms*	*Ohms*	*Ohms/degree*	*°C*
N_2=0 [a]	−94.950	15.7212	0.0000		0.000
"Pure" [b]		15.7176	.0036	0.10509	.034
"Pure"+*o*-xylene		15.5094	.2118	.10514	2.014
"Pure"+unknown		15.5360	.1853	.10514	1.762
***p*-XYLENE**					
N_2=0 [a]	13.260	26.8621	0.0000		0.000
"Pure" [b]		26.8411	.0210	0.10116	.208
"Pure"+*o*-xylene		26.5995	.2626	.10120	2.595
"Pure"+unknown		26.6547	.2074	.10119	2.050
***m*-XYLENE**					
N_2=0 [a]	−47.890	20.6183	0.0000		0.000
"Pure" [b]		20.4836	.1347	0.10314	1.306
"Pure"+*o*-xylene		20.2735	.3448	.10318	3.342
"Pure"+unknown		20.3611	.2572	.10316	2.493
***o*-XYLENE**					
N_2=0 [a]	−25.190	22.9503	0.0000		0.000
"Pure" [b]		22.9271	.0232	0.10234	.227
"Pure"+*p*-xylene		22.7149	.2354	.10238	2.299
"Pure"+unknown		22.7489	.2014	.10237	1.967
BENZENE					
N_2=0 [a]	5.530				

See footnotes at end of table.

TABLE 1.—*Experimental data on the determination of the four C_8 aromatics in an unknown mixture of aromatics*—Continued

Material	*A*	*B*	m_p/m_s	M_s/M_p	N_p	N_s	N_u
ETHYLBENZENE							
	Degree^{-1}	*Degree*$^{-1}$			*Mole fraction*	*Mole fraction*	*Mole fraction*
$N_2=0$ [a]	0.03454	0.00424			1.0000		
"Pure" [b]					0.9988		
"Pure"+*o*-xylene			13.871	1.0000	.9988	0.9322	0.0090
"Pure"+unknown			14.072	1.0085	.9988	.9405	.1136
***p*-XYLENE**							
$N_2=0$ [a]	0.02509	0.00276			1.0000		
"Pure" [b]					0.9948		
"Pure"+*o*-xylene			16.099	1.0000	.9948	0.9365	−0.0012
"Pure"+unknown			17.236	1.0085	.9948	.9496	.1641
***m*-XYLENE**							
$N_2=0$ [a]	0.02761	0.00337			1.0000		
"Pure" [b]					0.9644		
"Pure"+*o*-xylene			16.762	1.0000	.9644	0.9109	0.0138
"Pure"+unknown			16.334	1.0085	.9644	.9329	.4142
***o*-XYLENE**							
$N_2=0$ [a]	0.02660	0.00312			1.0000		
"Pure" [b]					0.9940		
"Pure"+*p*-xylene			17.442	1.0000	.9940	0.9403	0.0034
"Pure"+unknown			17.091	1.0085	.9940	.9487	.1688
BENZENE							
$N_2=0$ [a]	0.01523	0.00274			1.0000		

[a] This row, labeled $N_2=0$, gives values for the substance with zero impurity, that is, having $N_2=0$, where N_2 is the sum of the mole fractions of all the impurities. The indicated freezing point for zero impurity is the accepted value, taken from the tables of the API Research Project 44 at the National Bureau of Standards.

[b] This row, labeled "Pure", gives values for the material actually used for the "Pure" sample. Its purity is given in the column headed N_p.

The molecular weight of the unknown, determined from the lowering of the freezing point in benzene, is 107.31, which is to be compared with the value 107.06 determined from the data of the analytical distillation. In a check experiment, the molecular weight of a sample of pure ethylbenzene was determined from the lowering of the freezing point in benzene to be 106.45, as compared with the theoretical value of 106.16. The sum of the percentages of the four C_8 aromatics was determined to be 86.1 $\pm$2.4 percent by volume by measurement of freezing points, which value is to be compared with 85.0 $\pm$0.5 percent by volume obtained from the data of the analytical distillation. The amount of *o*-xylene determined by measurement of freezing points is 16.9 $\pm$1.2 percent by volume, which is to be compared with the value 17.6 $\pm$1.0 percent by volume obtained from the data of the analytical distillation.

Figure 1 shows a time-temperature freezing curve used to determine the freezing point of a solution of the unknown in *o*-xylene. Figure 2 shows a time-temperature melting curve used to determine

the freezing point of a solution of the unknown in ethylbenzene. Figure 3 shows a time-temperature freezing curve used to determine the freezing point of a solution of the unknown in benzene, for the determination of molecular weight.

V. DISCUSSION

From the results of the data so far obtained, it appears that, with the method and procedure described here, individual aromatic hydrocarbons can be determined in a mixture of aromatic hydrocarbons with an uncertainty for each compound near ±1 percent of the sample.

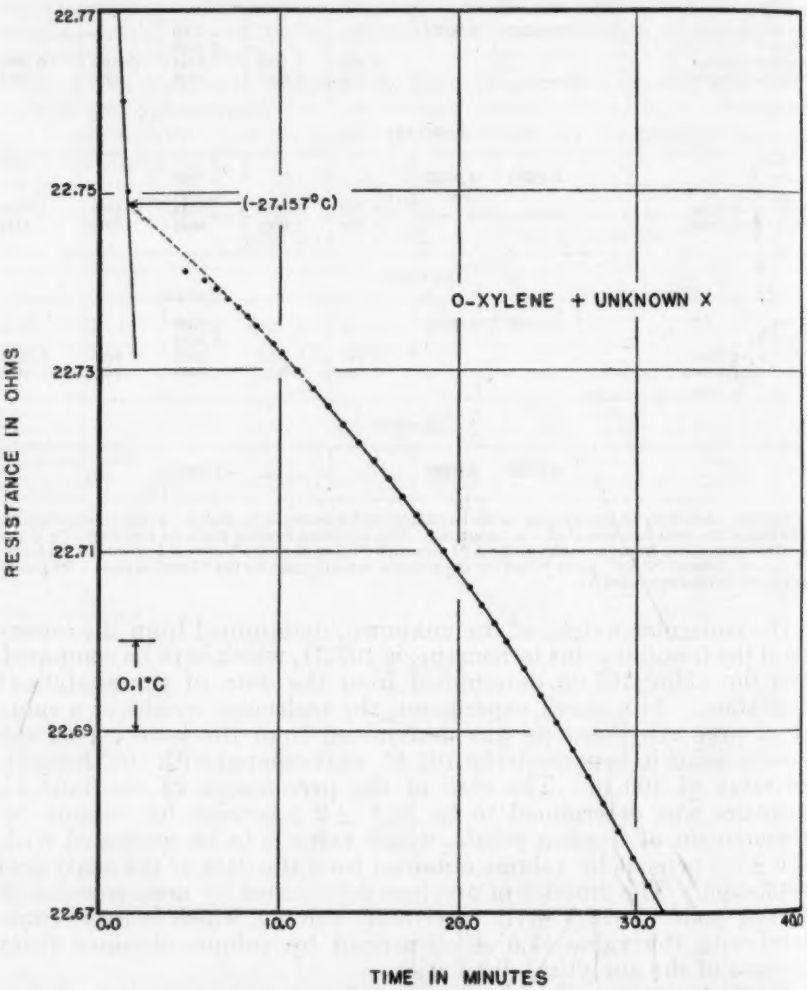

FIGURE 1.—*Time-temperature freezing curve for o-xylene plus an "unknown" mixture of aromatic hydrocarbons.*

The scale of ordinates gives the resistance of the platinum resistance thermometer in ohms. The scale of abscissas gives the time in minutes.

Previous measurements [3] have shown that mixtures of paraffins and cycloparaffins in dilute solution follow the ideal solution law of the lowering of the freezing point. It follows, therefore, that the present method can be used to determine individual paraffin or cycloparaffin hydrocarbons in mixtures of paraffin and cycloparaffin hydrocarbons.

Although no information is available with regard to olefin hydrocarbons and other types, there appears to be no reason why the method can not be used to determine individual olefins in a mixture of olefins, etc.

When the present investigation was nearing conclusion, references were found to the following three papers in the literature that men-

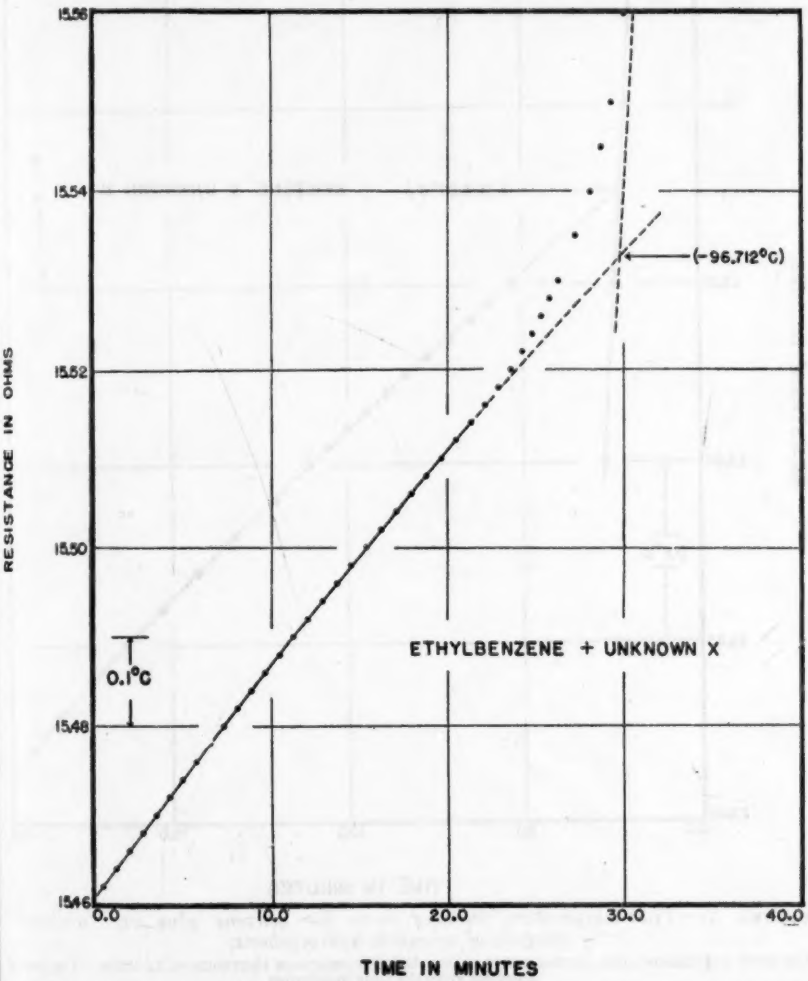

FIGURE 2.—*Time-temperature melting curve for ethylbenzene plus an "unknown" mixture of aromatic hydrocarbons.*

The scale of ordinates gives the resistance of the platinum resistance thermometer in ohms. The scale of abscissas gives the time in minutes.

tion or describe a method of analysis similar in principle to that described in the present paper: Norris and Rubinstein [5], Norris and Vaala [6], and Ibing [7]. The first two of these papers [5, 6] are concerned with other problems and barely mention the method. In the third paper, Ibing [7] describes his procedure and apparatus in detail, uses in his calculations only the simple limiting form of the law of the lowering of the freezing point, and does not define the freezing point nor tell how he determined it from his time-temperature observations.

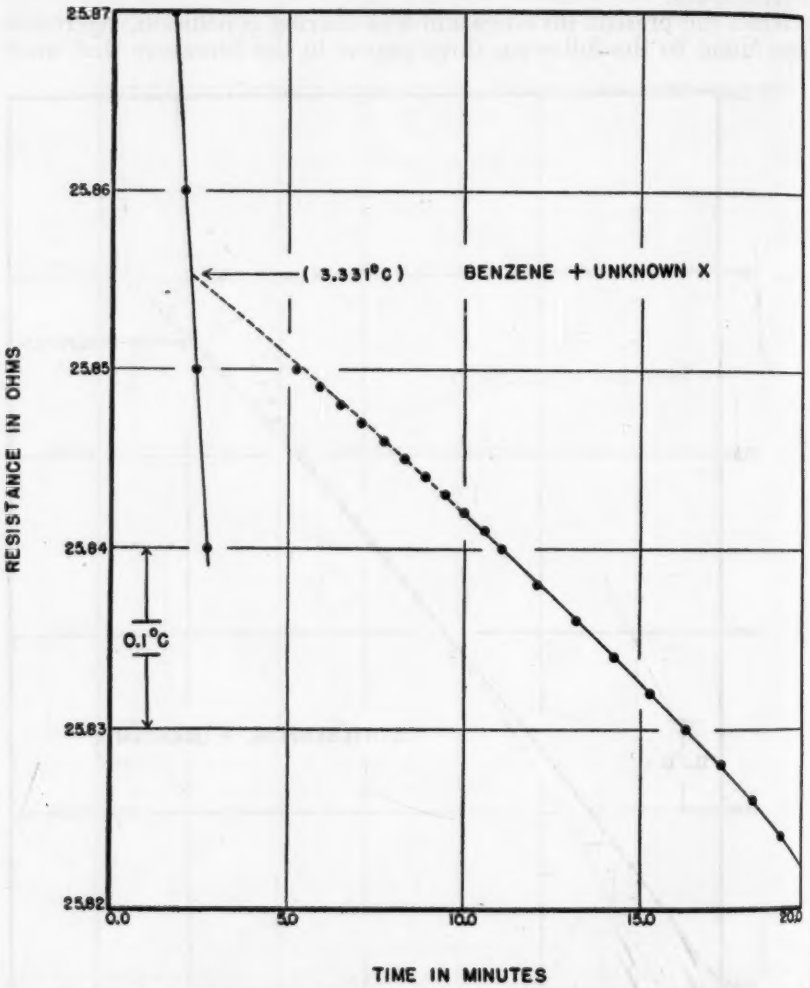

FIGURE 3.—*Time-temperature freezing curve for benzene plus an "unknown" mixture of aromatic hydrocarbons.*

The scale of ordinates gives the resistance of the platinum resistance thermometer in ohms. The scale of abscissas gives the time in minutes.

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WASHINGTON, January 8, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1585

Part of Journal of Research of the National Bureau of Standards, Volume 32, May 1944

THEORETICAL ANALYSIS OF CERTAIN TIME-TEMPERATURE FREEZING AND MELTING CURVES AS APPLIED TO HYDROCARBONS [1] [2]

By William J. Taylor [3] and Frederick D. Rossini

ABSTRACT

A method is described for determining analytically or graphically, from appropriate time-temperature freezing and melting curves obtained on hydrocarbons, the freezing point of a given substance, and within certain wide limits, the freezing point of that substance for zero impurity (liquid-soluble, solid-insoluble).

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I. INTRODUCTION

In a recent paper [1] [4] dealing with time-temperature freezing and melting curves obtained on hydrocarbons, it was shown how, when significant undercooling occurs on freezing, the observations can be analyzed to yield, in proper relation to the subsequent equilibrium part of the curve, the "zero" time, that is, the time at which crystallization would have begun in the absence of undercooling. In that paper, visual extrapolation of the equilibrium part of the curve, to "zero" time on freezing and to the corresponding time on melting, was used to determine the freezing point, defined as the temperature at which

[1] This investigation is part of the work on Research Project 44 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Presented before the Division of Petroleum Chemistry at the meeting of the American Chemical Society at Cleveland, Ohio, April 5, 1944.

[3] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[4] Figures in brackets indicate the literature references at the end of this paper.

an infinitesimal amount of crystals of the major component is in equilibrium with the liquid.[5]

The present paper describes a method, which may be used analytically or graphically, for extrapolating the equilibrium part of a time-temperature freezing or melting curve to give the freezing point, T_f, of the given hydrocarbon substance. There is also included a description of a method for deducing, within certain wide limits, from the same observations on the given substance if carried over a sufficiently large fraction of material crystallized or melted, the freezing point for zero impurity, T_{f_0}. When the heat of fusion is known or can be estimated, the value of $T_{f_0}-T_f$ serves to give the amount of liquid-soluble, solid-insoluble impurity in the given substance.

II. DERIVATION OF THE BASIC EQUATIONS

The definitions, abbreviations, and symbols used in this paper will be exactly the same as those of the previous paper [1], except that the subscript f attached to the time z, as in z_f, denotes the time corresponding to the freezing point, T_f. Some of the previous definitions and equations are repeated below for the sake of clarity and emphasis.

For an ideal, or a sufficiently dilute solution, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase, for the equilibrium between a liquid phase consisting of a major component and one or more other components and a crystalline phase of the major component alone, is [2, 3]

$$-\ln N_1=-\ln (1-N_2)=N_2(1+1/2N_2+\ \ldots)=$$

$$(\Delta H_{f_0}/RT_{f_0}^2)(T_{f_0}-T)[1+(1/T_{f_0}-\Delta C_{p_0}/2\Delta H_{f_0})(T_{f_0}-T)+\ \ldots]. \quad (1)$$

In eq 1, the symbols are defined as follows:

N_1 = the mole fraction of the major component in the liquid phase;
$N_2=(1-N_1)$ = the sum of the mole fractions of all other components in the liquid phase;
R = the gas constant, per mole;
T_{f_0} = the absolute temperature of the freezing point of the major component when pure (that is, when $N_1=1$ or $N_2=0$);
ΔH_{f_0} = the heat of fusion, per mole, of the major component in the pure state at the temperature T_{f_0};
ΔC_{p_0} = the heat capacity per mole, of the pure liquid less that of the pure solid, for the major component in the pure state at the temperature T_{f_0}; and
T = the given temperature of equilibrium.

The assumptions involved in the derivation of eq 1 are the following:

(a) The liquid solution is ideal, or sufficiently dilute, so that the fugacity of the major component in the liquid phase is proportional to its mole fraction.

(b) The heat of dilution is negligible over the range of concentration from $N_1=1$ to the given value of N_1.

[5] It is important to note that this temperature, when properly measured, must have the same value whether approached from a higher temperature as in cooling or from a lower temperature as in warming.

(c) The heat of fusion of the major component in the pure state at the temperature T may be represented by a power series expansion, as

$$\Delta H_f = \Delta H_{f_0} + \Delta C_{p_0}(T - T_{f_0})[1 + \ldots]. \tag{2}$$

Introducing the following additional abbreviations,

$$A = \Delta H_{f_0}/RT_{f_0}^2, \text{ and } B = 1/T_{f_0} - \Delta C_{p_0}/2\Delta H_{f_0}, \tag{3}$$

expanding $-\ln(1-N_2)$, and rearranging, eq 1 becomes

$$T_{f_0} - T = \frac{N_2}{A}[1 + 1/2N_2 + \ldots] - [B(T_{f_0} - T)^2 + \ldots]. \tag{4}$$

Neglecting terms in N_2^3 and higher, eq 4 becomes

$$T_{f_0} - T = \frac{N_2}{A}[1 + 1/2N_2 + \ldots] - \left[B\left(\frac{N_2}{A}\right)^2 + \ldots\right] \tag{5}$$

or

$$T_{f_0} - T = \frac{N_2}{A}[1 + (1/2 - B/A)N_2 + \ldots]. \tag{6}$$

In a system of the type under investigation, in which the solid phase is restricted to the major component, let n_1^* represent the total number of moles of the major component (in both the liquid and solid phases), n_2 represent the total number of moles of the other components (in the liquid phase), and n_1 represent the number of moles of the major component in the liquid phase under given conditions. Then the number of moles of the major component in the crystalline phase under the same conditions is $n_1^* - n_1$. Let r denote the fraction crystallized of the total number of moles of all components, that is,

$$r = (n_1^* - n_1)/(n_1^* + n_2). \tag{7}$$

The mole fraction, in the liquid phase, of the sum of all components other than the major components is defined by

$$N_2 = n_2/(n_1 + n_2). \tag{8}$$

Let N_2^* represent the value of N_2 when no crystalline phase is present, that is, when $n_1 = n_1^*$. Then

$$N_2^* = n_2/(n_1^* + n_2). \tag{9}$$

Combination of eq 7, 8 , and 9 yields the following equation relating N_2 and r:

$$N_2 = N_2^*/(1-r). \tag{10}$$

Letting

$$a = N_2^*/A, \text{ and } b = (1/2 - B/A)(N_2^*)^2/A, \tag{11}$$

and combining eq 10 and 6, there is obtained

$$T = T_{f_0} - \frac{a}{1-r} - \frac{b}{(1-r)^2} - \ldots = T_{f_0} - \frac{a}{1-r}\left[1 + \frac{b/a}{1-r} + \ldots\right]. \tag{12}$$

It is possible to further simplify eq 12 by using the general relation that, when

$$\left(\frac{b/a}{1-r}\right)^2<1,$$

$$\frac{a}{\left(1-\frac{b}{a}\right)-r}=\frac{a}{1-r}\left[1-\frac{b/a}{1-r}\right]^{-1}=\frac{a}{1-r}\left[1+\frac{b/a}{1-r}+\ \ldots\right]. \tag{13}$$

Assuming that the unwritten terms in eq 12 and 13 are negligible, or may be substituted one for the other without significant error, then eq 12 may be written

$$T=T_{f_0}-\frac{a}{\left(1-\frac{b}{a}\right)-r}\cdot \tag{14}$$

In general, the fractional error introduced by making the approximations leading to eq 14 will be of the order of 1/12 to 1/3 N_2^2, depending upon the value of B/A (see eq 3 and 4). That is to say, fractional errors in N_2, or correspondingly in $T_{f_0}-T$, will be about 1/3 to 1 1/3 percent when $N_2=0.2$, and about 1/12 to 1/3 percent when $N_2=0.1$. Equation 14 therefore would appear to be practically useful only when the amount of solute or impurity is below several tenths in mole fraction.

The next step is to express r, the fraction crystallized or melted, in terms of the time. This is done by assuming that the experiment is one in which the rate of crystallization or melting of the major component is constant with time.[6]

Denoting the time by the symbol z, and letting $z=z_f$ when $r=0$, one has the relation

$$r=k(z-z_f), \tag{15}$$

where k is a constant characteristic of the experiment, positive in sign for a freezing experiment and negative for a melting experiment. The time at which freezing begins, or melting is complete, is z_f, provided thermodynamic equilibrium is maintained throughout the experiment. The determination of z_f for an actual experiment has been discussed in reference [1].

Combination of eq 14 and 15 yields the following relation between the time and the temperature of equilibrium:

$$T=T_f-\frac{a'}{1-k'(z-z_f)}, \tag{16}$$

where $a'=a/(1-b/a)$ and $k'=k/(1-b/a)$.

Equation 16 relating T and z and eq 14 relating T and r are the equations of a rectangular hyperbola. The asymptote obtained by setting $z=-\infty$ in eq 16 is $T=T_{f_0}$.

Since there are three constants in eq 16, it is clear that three points on a portion of the curve satisfying eq 16 are sufficient to determine the values of the three constants, T_{f_0}, a', and k'. However, if it is

[6] This is essentially the case in experiments performed with the apparatus described in reference [1] when the range of freezing (or melting) temperature is sufficiently small in comparison with the head of temperature.

desired to test the accuracy with which the data satisfies the equation, a greater number of points are necessary.

The following theorem concerning a rectangular hyperbola will be required. Consider any four points (T_1, z_1), (T_2, z_2), (T_3, z_3) and T_4, z_4), on the hyperbola defined by eq 16. There are three ways in which two chords can connect these points, each point being the terminus of only one chord. These are illustrated in figure 1, in which m_{12} denotes the slope of the chord connecting points (T_1, z_1) and (T_2, z_2), and similarly for m_{13}, m_{23}, and m_{14}. It is to be shown that the products of the slopes of the two chords is the same in each of the three cases

$$m_{12}m_{34}=m_{13}m_{24}=m_{14}m_{23}. \tag{17}$$

Using eq 16,

$$m_{12}=\left(\frac{T_2-T_1}{z_2-z_1}\right)=\frac{-a'k'}{[1-k'(z_1-z_f)][1-k'(z_2-z_f)]} \tag{18}$$

and

$$m_{12}m_{34}=\frac{(a'k')^2}{[1-k'(z_1-z_f)][1-k'(z_2-z_f)][1-k'(z_3-z_f)][(1-k'(z_4-z_f)]} \tag{18a}$$

Equation 17 follows immediately, since the expression on the right-hand side of eq 18a is unchanged in value by any interchange of the subscripts 1, 2, 3, and 4.

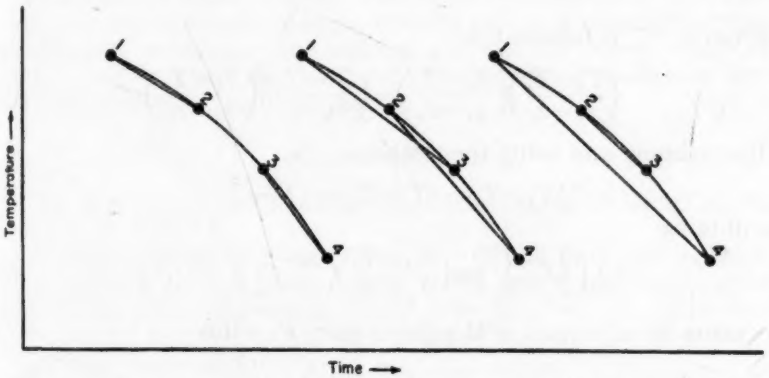

FIGURE 1.—*Construction to show three ways of connecting four points on a curve with two chords, with each point being the terminus of only one chord.*

III. DETERMINATION OF THE FREEZING POINT

1. ANALYTICAL

The procedure for determining the freezing point of the given substance analytically from the equilibrium portion of the time-temperature curve is illustrated by means of figure 2. Points G, H, and I are on the equilibrium part of the time-temperature curve, as defined by eq 16. The zero time, at which crystallization would have begun in the absence of undercooling, has been determined [1]. It is required to determine on the ordinate through the zero time, z_f, the freezing point T_f.

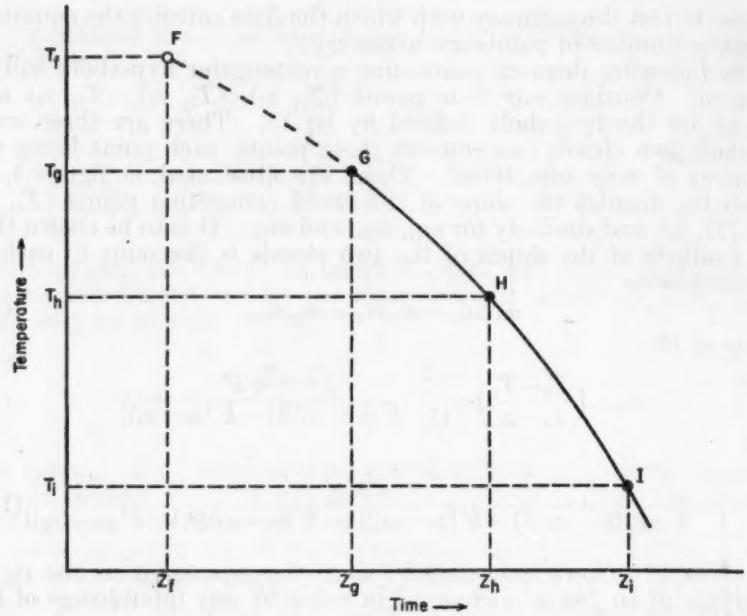

FIGURE 2.—*Construction to show the analytical determination of the freezing point.*

From eq 17, it follows that

$$\left(\frac{T_f-T_g}{z_g-z_f}\right)\left(\frac{T_h-T_i}{z_i-z_h}\right)=\left(\frac{T_f-T_i}{z_i-z_f}\right)\left(\frac{T_g-T_h}{z_h-z_g}\right). \tag{19}$$

Rearranging and using the relation

$$(T_f-T_i)=(T_f-T_g)+(T_g-T_i), \tag{20}$$

one obtains

$$1+\left(\frac{T_g-T_i}{T_f-T_g}\right)=\left(\frac{T_h-T_i}{T_g-T_h}\right)\left(\frac{z_h-z_g}{z_i-z_h}\right)\left(\frac{z_i-z_f}{z_g-z_f}\right). \tag{21}$$

Denoting by u, v, and w the dimensionless ratios

$$u=\left(\frac{T_h-T_i}{T_g-T_h}\right) \tag{22}$$

$$v=\left(\frac{z_h-z_g}{z_i-z_h}\right) \tag{23}$$

$$w=\left(\frac{z_i-z_f}{z_g-z_f}\right), \tag{24}$$

there is obtained, on substitution into eq 21, the relation

$$T_f=T_g+\left(\frac{T_g-T_i}{uvw-1}\right). \tag{25}$$

Equation 25 gives the value of T_f, when there are known the temperature and time corresponding to three points (as G, H, and I) on the equilibrium curve (as defined by eq 14) and the "zero" time, the time

at which crystallization would have begun in the absence of undercooling.[7]

It is nearly always possible to select the point H equidistant in time between G and I, so that $v=1$. Furthermore, it will usually be possible to space the points G, H, and I so that w is a simple ratio. Thus, if all three time intervals are equal

$$\left.\begin{aligned}(z_g-z_f)=(z_h-z_g)=(z_i-z_h)\\ v=1\\ w=3\\ T_f=T_g+(T_g-T_i)/(3u-1)\end{aligned}\right\}. \tag{26}$$

When the first time interval is twice as great as the other two intervals, then

$$\left.\begin{aligned}(z_g-z_f)=2(z_h-z_g)=2(z_i-z_h)\\ v=1\\ w=2\\ T_f=T_g+(T_g-T_i)/(2u-1)\end{aligned}\right\}. \tag{27}$$

It is obvious that a large value of w corresponds to a short extrapolation to T_f, and vice versa.

Although the curve in figure 2 has been drawn to simulate a freezing curve, the above equations apply equally well to a melting curve, since, for the same substance, the melting curve is the mirror image of the freezing curve when the time rate of melting is made the same as the time rate of crystallization.

2. GEOMETRICAL

The manner of determining geometrically the freezing point, T_f, is shown in figure 3.

There are given the "zero" time, z_f, and the time and temperature corresponding to the three points, G, H, and I, on the equilibrium part of the time-temperature curve defined by eq 16. It is required to locate the freezing point, T_f, on the ordinate at the time z_f.

The solution is as follows:

Draw $\overline{AB}$ through I parallel to the time axis.

Draw $\overline{AC}$ perpendicular to $\overline{AB}$, at the time z_f.

Draw a line through points G and H, intersecting $\overline{AB}$ at E and $\overline{AC}$ at D.

Draw a line through points I and H, intersecting $\overline{AC}$ at J.

Draw $\overline{JK}$ parallel to $\overline{DE}$.

Draw a line through points K and G, intersecting $\overline{AC}$ at F.

F is the desired point, representing the freezing point, T_f.

[7] It is worthwhile remarking that eq 25 is not limited to the determination of the freezing point, T_f. z_f in eq. 24 may be any given time, and eq. 25 then yields the corresponding temperature, T_f. It has been implied in the foregoing discussion that the cooling curve before crystallization begins (or the warming curve after melting is complete) is sufficiently steep so that z_f may be estimated exactly enough from a preliminary visual extrapolation to T_f. It is clear that if this is not the case, T_f may still be obtained with any required accuracy by successive applications of eq 25.

The proof, illustrated in figure 4, is as follows:

Draw $\overline{FI}$.

Draw $\overline{NP}$ through H, parallel to $\overline{AB}$.

Then

$$\overline{NH}/\overline{NP}=\overline{ND}/\overline{NJ} \tag{28}$$

But

$$\overline{AI}/\overline{AK}=\overline{NH}/\overline{NP}. \tag{29}$$

Therefore,

$$\overline{ND}/\overline{NJ}=\overline{AI}/\overline{AK}. \tag{30}$$

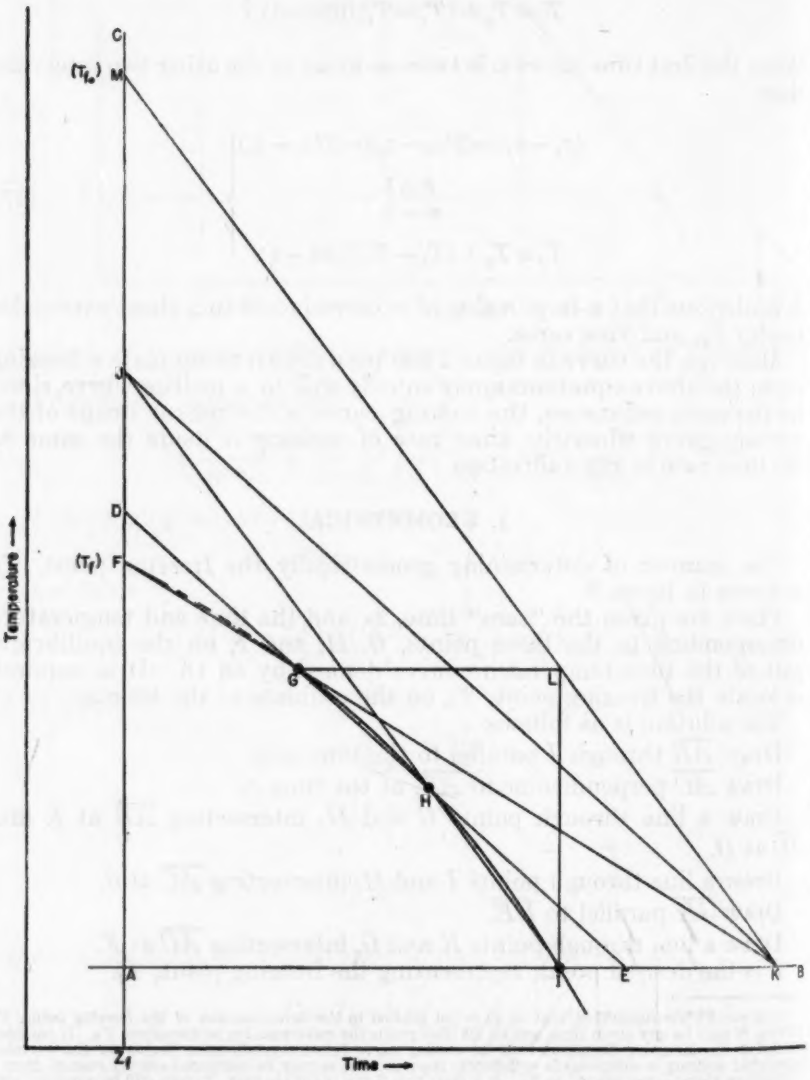

FIGURE 3.—*Geometrical construction for determining T_f and T_{f_0}.*

But, by eq 17,

$$(\overline{ND}/\overline{NH})(\overline{AF}/\overline{AI})=(\overline{AF}/\overline{AK})(\overline{NJ}/\overline{NH}), \quad (31)$$

which gives

$$\overline{ND}/\overline{NJ}=\overline{AI}/\overline{AK}, \quad (32)$$

in agreement with eq 30.

IV. DETERMINATION OF THE FREEZING POINT FOR ZERO IMPURITY

The method described here for determining the freezing point for zero impurity, T_{f_0}, can be properly applied only to those experiments

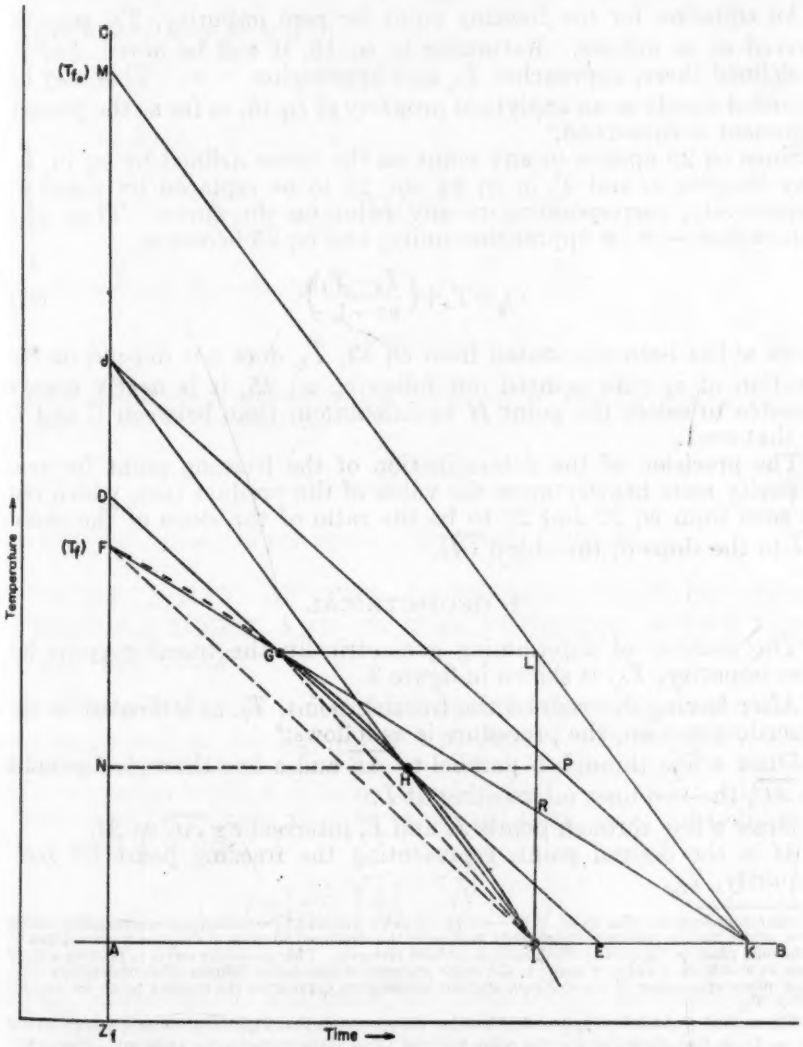

FIGURE 4.—*Proof of geometrical construction for determining T_f and T_{f_0}.*

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in which the time-temperature observations extend over a sufficiently large fraction (probably of the order of ¼ to ½) of material crystallized. Furthermore, since that portion of the curve which is required for determining T_{f_0} is also the portion in which departures will most likely occur in the relations upon which eq 16 is based, it is seen that the determination of even an approximate value of T_{f_0} will frequently be impossible for many experiments. However, for completeness, the description of the procedure for evaluating T_{f_0} by this method is given here so that it may be available for application to those experiments which do conform to the requirements.

1. ANALYTICAL

An equation for the freezing point for zero impurity, T_{f_0}, may be arrived at as follows. Returning to eq 16, it will be noted that T, as defined there, approaches T_{f_0} as z approaches $-\infty$. This may be regarded simply as an analytical property of eq 16, so far as the present argument is concerned.[8]

Since eq 25 applies to any point on the curve defined by eq 16, we may imagine z_f and T_f in eq 24 and 25 to be replaced by z and T, respectively, corresponding to any point on the curve. Then as z approaches $-\infty$, w approaches unity, and eq 25 becomes

$$T_{f_0}=T_g+\left(\frac{T_g-T_f}{uv-1}\right). \tag{33}$$

Since w has been eliminated from eq 33, T_{f_0} does not depend on the location of z_f. As pointed out following eq 25, it is nearly always possible to select the point H equidistant in time between G and I, so that $v=1$.

The precision of the determination of the freezing point for zero impurity rests heavily upon the value of the product (uv), which can be seen from eq 22 and 23 to be the ratio of the slope of the chord $\overline{HI}$ to the slope of the chord $\overline{GH}$.

2. GEOMETRICAL

The manner of determining geometrically the freezing point for zero impurity, T_{f_0}, is shown in figure 3.

After having determined the freezing point, T_f, as indicated in the preceding section, the procedure is as follows:[9]

Draw a line through G parallel to $\overline{AB}$ and a line through I parallel to $\overline{AC}$, the two lines intersecting at L.

Draw a line through points K and L, intersecting $\overline{AC}$ at M.

M is the desired point, representing the freezing point for zero-impurity, T_{f_0}.

[8] The extension of the time in eq 16 to $-\infty$ may be easily pictured by considering a corresponding melting curve, which may be prolonged indefinitely in time by the continued addition of the pure major component in the solid phase to the existing solid phase as melting proceeds. This procedure serves to produce a liquid phase in which the number of moles of the major component approaches infinity, the composition of the liquid phase approaches $N_1=1$ or $N_2=0$, and the temperature approaches the freezing point for zero impurity, T_{f_0}.

[9] The method of obtaining T_{f_0} described here has the advantage that T_{f_0} is obtained on the same vertical axis as T_f, so that the initial freezing point lowering $(T_{f_0}-T_f)$ is immediately apparent. However, it should be pointed out that the value of T_{f_0} obtained depends only on the points G, H, and I, and not at all on the time chosen for z_f.

The proof is as follows:

Draw $\overline{GI}$.

Since point F is on the curve, eq 22, 23, and 33, for T_{f_0}, may be rewritten with the three points G, H, and I replaced by F, G, and I.

$$T_{f_0}=T_f+\left(\frac{T_f-T_i}{u'v'-1}\right), \tag{34}$$

where

$$u'=\left(\frac{T_g-T_i}{T_f-T_g}\right) \tag{35}$$

$$v'=\left(\frac{z_g-z_f}{z_i-z_g}\right) \tag{36}$$

Equation 34 may be put in the form

$$\left(\frac{T_{f_0}-T_i}{T_{f_0}-T_f}\right)=u'v'. \tag{37}$$

But from figure 4,

$$\left(\frac{T_{f_0}-T_i}{T_{f_0}-T_f}\right)=\overline{AM}/\overline{FM}=\overline{IL}/\overline{RL}. \tag{38}$$

Also, from eq 35 and 36 and figure 4,

$$u'v'=m_{GI}/m_{FG}, \tag{39}$$

where m_{GI} and m_{FG} are the slopes of the chords $\overline{GI}$ and $\overline{FG}$, respectively. Combining eq 37, 38, and 39,

$$\overline{IL}/m_{GI}=\overline{RL}/m_{FG}. \tag{40}$$

But both sides of eq 40 are equal to $\overline{GL}$, from figure 4.

V. UNCERTAINTY OF THE DETERMINATION OF THE FREEZING POINT AND OF THE FREEZING POINT FOR ZERO IMPURITY

An expression may be derived for the error of T_f or T_{f_0}, as calculated from eq 25 and 33, for any given experiment. For simplicity, one may assume that there is no error in z_f, z_g, z_h, and z_i, but that a uniform random error, σ, is to be attached to T_g, T_h, and T_i (fig. 2). The error in T_f, σ_f, may then be calculated from the usual propagation of error equation

$$\left(\frac{\sigma_f}{\sigma}\right)^2=\left(\frac{\partial T_f}{\partial T_g}\right)^2+\left(\frac{\partial T_f}{\partial T_h}\right)^2+\left(\frac{\partial T_f}{\partial T_i}\right)^2. \tag{41}$$

Equation 41 assumes that the errors in T_g, T_h, and T_i are, on the average, uncorrelated, and gives the error for T_f in terms of the average of these errors, σ.

The derivatives in eq 41 may be obtained by differentiation of

eq 25, noting that u, but not v and w, is a function of T_g, T_h, and T_i. They may be put in the following form (with the aid of eq 22):

$$\left(\frac{\partial T_f}{\partial T_g}\right)=\frac{u^2vw(vw+1)}{(uvw-1)^2} \tag{42}$$

$$\left(\frac{\partial T_f}{\partial T_h}\right)=-\frac{vw(u+1)^2}{(uvw-1)^2} \tag{43}$$

$$\left(\frac{\partial T_f}{\partial T_i}\right)=\frac{(vw+1)}{(uvw-1)^2}. \tag{44}$$

When eq 42, 43, and 44 are substituted into eq 41, there is obtained the relation:

$$\left(\frac{\sigma_f}{\sigma}\right)^2=\frac{(vw+1)^2(u^4v^2w^2+1)+v^2w^2(u+1)^4}{(uvw-1)^4}, \tag{45}$$

which expresses (σ_f/σ) as a function of u, v, and w. Equation 45 may be put in a more useful form as follows:

For any given segment of an equilibrium curve, the greatest accuracy in T_f (minimum σ_f) will be obtained by choosing z_g and z_i at the beginning and end of the segment in question (corresponding to a maximum value of w). With z_g and z_i fixed, the following relation then holds:

$$uv=c, \tag{46}$$

where c is a constant characteristic of the given segment of the curve, and independent of the choice of z_h. Equation 46 may be derived in the following way.

It is evident from eq 22 and 23 that the product (uv) is the ratio of the slope of the chord $\overline{HI}$ to the slope of the chord $\overline{GH}$ (fig. 2) From eq 18 c is then given by

$$c=\left(\frac{1-k'z_g}{1-k'z_i}\right), \tag{47}$$

which is independent of z_h.

If one eliminates u from eq 45 and 46, there is obtained the relation

$$\left(\frac{\sigma_f}{\sigma}\right)^2=\frac{(vw+1)^2(c^4w^2+v^2)+w^2(c+v)^4}{v^2(cw-1)^4}. \tag{48}$$

A numerical investigation of eq 48 shows, as would be expected, that, for the range of conditions encountered in practice, the optimum value of v is in the neighborhood of unity (corresponding to z_h equidistant between z_g and z_i). When $v=1$, $u=c$, and eq 48 becomes

$$\left(\frac{\sigma_f}{\sigma}\right)^2=\frac{(w+1)^2(u^4w^2+1)+w^2(u+1)^4}{(uw-1)^4}. \tag{49}$$

The error in T_{f_0}, σ_{f_0}, may be obtained immediately by setting w equal to unity in eq 48 or 49. When $v=1$,

$$\left(\frac{\sigma_f}{\sigma}\right)^2=\frac{4(u^4+1)+(u+1)^4}{(u-1)^4}. \tag{50}$$

From eq 49, (σ_f/σ), for $v=1$, has been calculated for $w=1$, 1.5, 2, 3, 5, and ∞, and for $u=1$, 1.25, 1.5, 2, 3, 4, and ∞. The results are presented in figure 5, in which the abscissas represent $(1/u)$, and the ordinates represent (σ_f/σ), on a logarithmic scale. The curve for $w=1$ represents (σ_{f_0}/σ), and rises to infinity at $(1/u)=1$, which corresponds to a freezing curve of constant slope. The other curves, representing (σ_f/σ) for various values of w, are finite for all values of $(1/u)$.

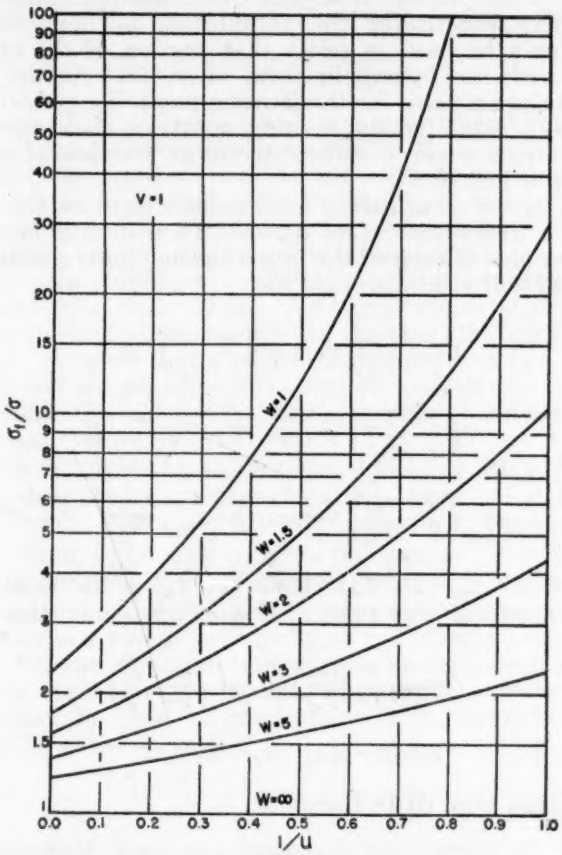

FIGURE 5.—*Chart to show the uncertainty of the determination of T_f and T_{f_0}.*

Figure 5 is expected to be convenient for estimating the uncertainties of T_f and T_{f_0} in practice. In calculating T_f and T_{f_0} from eq 25 and 33, u and w are first evaluated from eq 22 and 24 $(v=1)$. The values of (σ_f/σ) and (σ_{f_0}/σ)may then be read immediately from figure 5. It remains for the experimenter to estimate a reasonable value for σ. In any case, figure 5 indicates relative errors for various values of u and w.

The errors discussed above do not include those arising from departures from the ideal solution laws or from lack of constancy of the rate of crystallization or melting (see appendix, page 212.)

VI. ALTERNATIVE METHOD FOR DETERMINING THE FREEZING POINT (AND THE FREEZING POINT FOR ZERO IMPURITY)

The foregoing methods for determining T_f (and, where appropriate, T_{f_0}) may be used when the experimenter is able from previous experience to select with some assurance the equilibrium portion of the time-temperature freezing or melting curve. When there is some doubt as to what portion, if any, of the time-temperature freezing or melting curve constitutes the equilibrium portion, the following procedure may be used to select that portion of the curve that is consistent with the hyperbolic form of eq 16. At the same time, there is obtained a value for the freezing point, T_f, and within certain wide limits, a value for the freezing point for zero impurity, T_{f_0}, if the observations cover a sufficiently large fraction of the material crystallized or melted.

Let (T_m, z_m) be an arbitrary fixed point chosen on the equilibrium portion of a time-temperature curve. Then it may be shown from eq 16 that a plot of each of the following functions against the variable indicated will yield a *straight line:*

$$\left(\frac{1}{T-T_m}\right) \text{ versus } \left(\frac{1}{z-z_m}\right)$$

$$\left(\frac{T-T_m}{z-z_m}\right) \text{ versus } (T-T_m), \text{ or } T$$

$$\left(\frac{z-z_m}{T-T_m}\right) \text{ versus } (z-z_m), \text{ or } z$$

The plot of $(z-z_m)/(T-T_m)$ versus $(z-z_m)$ is the most convenient for the purposes of this paper. Define new quantities y and x as follows:

$$y=\left(\frac{z-z_m}{T-T_m}\right); \; y_f=\left(\frac{z_f-z_m}{T_f-T_m}\right) \tag{51}$$

$$x=(z-z_m); \quad x_f=(z_f-z_m) \tag{52}$$

Then it follows from eq 16 that

$$y=y_0+sx; \; y_f=y_0+sx_f \tag{53}$$

where

$$s=\left(\frac{1}{T_{f_0}-T_m}\right). \tag{54}$$

$$y_0=-\left(\frac{(a'/k')}{(T_{f_0}-T_m)^2}\right) \tag{55}$$

Thus a plot of y against x yields a straight line for that portion of the curve, presumably the equilibrium portion, which is consistent with eq 16. Extrapolation of the straight line to $x=x_f(z=z_f)$,

yields y_f; T_f may then be calculated from the equation

$$T_f = T_m + \frac{x_f}{y_f}, \tag{56}$$

similarly,

$$T_{f_0} = T_m + 1/s = T_m + \frac{y_f - y_m}{x_f}, \tag{57}$$

since $x_m = 0$. The smoothed temperature at any other time is given by the relation

$$T = T_f - \frac{x_f}{y_f} + \frac{x}{y}. \tag{58}$$

The point (T_m, z_m) should be selected near the middle of that portion of the time-temperature curve which the experimenter regards as most likely to represent equilibrium. The linearity of the y versus x plot is then an indication of the range on either side of (T_m, z_m) in which equilibrium has apparently been maintained. It should be noted that the error in the calculated value of y increases rapidly as x decreases. In plotting y it is better to plot circles, of radii inversely proportional to x, than points. This will insure approximately the correct weighting of the points in drawing the straight line. It should also be noted that a slight displacement of (T_m, z_m) from the true curve will have a negligible effect on the location of the straight line, provided (T_m, z_m) is about in the middle of the equilibrium portion of the curve.

Equation 57 relates T_{f_0} to the slope, s, of the y versus x plot. However, it is clear that s is a sort of second derivative of the time-temperature curve. It is to be expected, therefore, that the value of T_{f_0} calculated from eq 57 may be quite inaccurate. It is possible to reverse the procedure, if T_{f_0} is known, and calculate the value of the slope of the y versus x plot to be expected on the basis of eq 16.

The y versus x plot is principally of use in extrapolating to obtain T_f, by eq 56, and also in obtaining smoothed values of the temperature at any other time, by eq 58. The smoothed values of the temperature may be used in conjunction with the other methods of obtaining T_{f_0} as described [1].

[1].

VII. DISCUSSION

In connection with the practical application of the foregoing methods for determining from time-temperature freezing and melting curves the freezing point, T_f, and the freezing point for zero impurity, T_{f_0}, the following points are important:

(a) The experimenter must assure himself that the time-temperature relations substantially follow eq 16 over that part of the experiment which represents thermodynamic equilibrium between the liquid and solid phases. (See section VI and the appendix of this paper.)

(b) The precision of determining the freezing point, T_f, will be nearly as good as the determination of temperatures along the equilibrium part of the curve, except when the time and temperature

covered by undercooling are very large. In terms of the uncertainty in the temperatures along the equilibrium part of the curve, the untainty in T_f is given by eq 49 and illustrated in figure 5.

(c) The precision of determining the freezing point for zero impurity, T_{f_0}, by the method described, will be much less precise than the determination of the freezing point. In terms of the uncertainty in the temperatures along the equilibrium portion of the curve, the uncertainty in T_{f_0} is given by eq 50 and illustrated in figure 5 by the curve for which $w=1$. The practical utility of determining T_{f_0} by this method depends entirely upon the equilibrium portion of the curve covering a sufficiently large range of r (fraction crystallized, or melted) so that the product uv in eq 33, the ratio of the slopes of the two chords, will have a value appreciably greater than unity. If the observations of the given experiment do not cover a sufficiently large fraction of material crystallized or melted, no useful determination of T_{f_0} may be made by this method. For any given experimental procedure, it is desirable to check the value of T_{f_0} obtained by this method with the value obtained by the method previously described [1], which has been shown to give reliable results.

VIII. REFERENCES

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IX. APPENDIX

In the foregoing discussions, it has been assumed for simplicity that the rate of crystallization is a constant, or that r is linear in z, as given by eq 15. It is of interest to consider the effect of a varying rate of crystallization. Two types of variation may be distinguished:

(a) The rate of crystallization varies initially, but approaches a constant value as the experiment proceeds.

(b) The rate of crystallization varies progressively as the experiment proceeds, and does not tend to approach a constant value. Supercooling should give rise to a variation of type (a). Variations of type (a) will destroy, for a certain time, the rectangular hyperbolic relation between T and z, eq 16, on which the linearity of the $(z-z_m)/(T-T_m)$ versus$(z-z_m)$ plot depends. It may therefore be assumed that in the linear region of this plot such variations have decreased sufficiently to be neglected.

Variations of type (b) are of more importance, since they increase throughout the experiment. Such variations would be caused, for example, by any factor, such as a decreasing (or increasing) head of temperature, that alters the rate of heat transfer and hence the rate of crystallization (or melting).

If the variation is of type (b), r may be represented by a power series in $(z-z_f)$:

$$r=k(z-z_f)[1-e(z-z_f)+\ .\ .\ .]. \tag{59}$$

Now consider the following expansion, valid for $[e(z-z_f)]^2$ less than unity:

$$\left[\frac{k(z-z_f)}{1+e(z-z_f)}\right]=k(z-z_f)[1-e(z-z_f)+\ .\ .\ .]. \tag{60}$$

Therefore, when the higher order terms in eq 59 and 60 may be neglected, r may be written:

$$r=\frac{k(z-z_f)}{1+e(z-z_f)}. \tag{61}$$

Equation 61 is a rectangular hyperbolic relation between r and z. Furthermore, eq 14 is a rectangular hyperbolic relation between T and r. It is easily shown that the relation between T and z obtained by substitution of eq 61 in eq 14 is also rectangular hyperbolic. Specifically, eq 16 is replaced by the equation:

$$T=\left(T_{f_0}+\frac{a'e}{k'-e}\right)-\frac{a'k'/(k'-e)}{1-(k'-e)(z-z_f)}. \tag{62}$$

Equation 62 reduces to eq 16 for e equal to zero.

It is clear from eq 62 that all the results previously derived on the basis of eq 16 are unchanged, provided k' is replaced by $(k'-e)$, a' is replaced by $[a'k'/(k'-e)]$, and T_{f_0} is replaced by $[T_{f_0}+a'e/(k'-e)]$. Of the previous results which are unaffected, there may be mentioned the theorem concerning the slopes of the chords, eq 17, and the linearity of the $(z-z_m)/(T-T_m)$ versus $(z-z_m)$ plot. The calculated value of T_f will not be in error. However, the calculated value of T_{f_0} will be in error by the amount $[a'e/(k'-e)]$, corresponding to the fact that the asymptote of the hyperbola is shifted.

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A METHOD FOR THE DETERMINATION OF THE pH OF 0.05-MOLAL SOLUTIONS OF ACID POTASSIUM PHTHALATE WITH OR WITHOUT POTASSIUM CHLORIDE

By Walter J. Hamer and S. F. Acree

ABSTRACT

The pH values of a 0.05-*m* solution of acid potassium phthalate containing various amounts of potassium chloride were determined at 5-degree intervals from 0° to 60° C, inclusive, from the measurements of the electromotive force of galvanic cells without liquid junction using hydrogen and silver-silver-chloride electrodes. A method is described for the determination of the pH directly from the emf by means of the equation

$$\mathrm{pH}=[(E-E^\circ)/(RT/F)+\log m_{\mathrm{Cl}}-P]/Q,$$

where P and Q are constants whose numerical values depend on the ionic strength of the solution and the nature of the cation and E°, R, T, and F have their usual significance. By this method a 0.05-*m* solution of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, is found to have a pH of 4.008 at 25° C, and this value does not vary much with the temperature. A description is also given of the application of the method to the determination of the pH and the ionic strength of unknown solutions of low salt content.

Equations were formulated to express the variation of the pH of a 0.05-*m* solution of acid potassium phthalate with temperature and with the concentration of potassium chloride. The pH values may be computed for temperatures from 0° to 60° C, inclusive, by the equation

$$\mathrm{pH}=5.13\log T+1519.62/T+0.01092\,T-17.039,$$

where $T=t^\circ\ \mathrm{C}+273.16$. The pH values for concentrations of potassium chloride from 0 to 0.05 *m* may be computed by the equation

$$\mathrm{pH}_{\text{with salt}}=\mathrm{pH}_{\text{without salt}}-0.993m_{\mathrm{KCl}}+2.124m_{\mathrm{KCl}}^2.$$

The solutions may be readily prepared from known weights of acid potassium phthalate, potassium chloride, and distilled water and are well suited for use as pH standards, in that their pH values do not change much with temperature or dilution.

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I. INTRODUCTION

Buffer solutions prepared with acid potassium phthalate are extensively used for the calibration of commercial pH meters and other pH equipment. A 0.05-*m* solution is generally employed and

conveniently prepared from the dry salt and distilled water. The pH value of this solution has usually been determined from the measurements of galvanic cells comprised of various types of hydrogen and calomel electrodes. By this method, pH values ranging from 3.92 to 4.01 [1 to 4] [1] have been reported for a temperature of 25° C. The differences in these pH values are due partly to lack of equilibrium of the galvanic cell [5, 6, 7], partly to liquid-junction errors [8 to 12] arising from the use of calomel electrodes, and partly to the use of hydrogen-ion concentration rather than hydrogen-ion activity as the basis of the definition of the pH scale.[2] This paper gives a method for the determination of the pH of a 0.05–*m* solution of acid potassium phthalate from the measurements of the emf of galvanic cells without liquid junction. The effect of varying amounts of potassium chloride upon the pH of a 0.05–*m* solution of acid potassium phthalate is also given. The latter data are included because they give information concerning the activity coefficients of the ions composing the mixture.[3] A description is also given of the application of the method to the determination of the pH values and ionic strengths of unknown solutions of low salt content [24].

II. EXPERIMENTAL PROCEDURE

The method is based upon the measurements of the emf of the galvanic cell

$$\mathrm{Pd,\ H_2(g)|KHPh(0.05\ }m\mathrm{),\ KCl(}m\mathrm{)|AgCl(s)|Ag(s)}$$

for a series of concentrations (m) of potassium chloride, in which KHPh designates acid potassium phthalate, and the other symbols have their usual significance.

The hydrogen electrodes used were made of platinum foil (10 by 15 by 0.2 mm), and were plated with a thin coat of palladium sponge by electrolysis of a 1-percent solution of palladium chloride containing a trace of lead acetate for 1 minute at a current density of 0.04 amp/cm^2 [5]. Electrodes of this type do not catalyze the reduction of acid potassium phthalate and function reversibly for well over 100 hours in solutions containing various amounts of potassium chloride. Silver–silver-chloride electrodes of the thermal-electrolytic type were prepared from pure materials, as described in a previous paper [13]. They were sufficiently aged to bring them to a stable state. Other equipment, including the cells, thermostat, and emf-recording instruments have been described in detail [13].

The acid potassium phthalate used was National Bureau of Standards Standard Sample 84a, having a certified purity of 100.00 percent,

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] It is well known that an exact differentiation between hydrogen-ion concentration and activity cannot be made, since the value of the activity coefficient of the hydrogen-ion cannot be determined without some assumption. Hitchcock and Taylor [3], and MacInnes, Belcher, and Shedlovsky [4] in their methods obtain a quantity which approximates the value of the hydrogen-ion activity. In the work on pH standards in this Bureau the assumption is made that the activity coefficient of the hydrogen-ion is equal to the mean activity coefficient of hydrochloric acid, a quantity which can be determined experimentally from electromotive-force measurements. See references [8, 13 to 15] for discussions of this assumption in connection with work on pH standards.

[3] If the dissociation of an acid salt conformed to the simple law of mass action for finite concentrations, the effect of a neutral salt on the dissociation of the acid salt could be determined solely from its concentration. However, as a result of ionic association, the nature of the medium, and salt effects, certain processes occur which lead to departures from ideality. For a review of the earlier studies of the effects of salts on the dissociation and reactions of weak electrolytes, see the paper by Burton, Hamer, and Acree [16]. See also the papers by Loomis and Acree [17] and Bronsted [18].

determined by titration. It was prepared for use according to the directions given in the Bureau certificate. Potassium chloride was recrystallized twice from conductivity water and then thrice by the addition of 95-percent ethanol to remove the last traces of bromide. It was dried for at least 10 hours at 110° C and allowed to cool in a desiccator, using concentrated sulfuric acid as the desiccant. The solutions were prepared from known weights of the dry salts and conductivity water. The concentrations were expressed in terms of weight of solute per 1,000 g of water. All the solutions were deaerated by means of purified hydrogen gas before they were introduced into the cells. Corrections were made for the loss of water from the solutions during the deaeration process and for the differences between the densities of hydrogen and air. The specific conductance of the water used in this work was generally 1.0×10^{-6} mho and sometimes was as low as 0.6×10^{-6} mho.

In table 1, the values of emf given were corrected in the usual manner to 1 atmosphere of hydrogen pressure. The results of triplicate (three) determinations (values) are given for 25° C and of duplicate determinations (two) for 45° C. The values of the emf were first recorded at 25° C. The bath was then cooled to 0° C in 5-degree steps and the emf recorded at each temperature. Then the temperature of the bath was raised to 25° C and the emf again recorded. The temperature of the bath was then raised to 60° C in 5-degree steps and the emf recorded at each temperature. Finally, the bath was cooled first to 45° C and then to 25° C and the emf measured at each temperature. The first and final emf at 25° C agreed within 0.09 mv, or 0.002 pH unit, on the average for the nine concentrations.

TABLE 1.—*Electromotive forces of the galvanic cell* Pd, H_2(g)|KHPh(0.05 *m*), KCl (*m*)|AgCl (s)|Ag (s) *from 0° to 60° C*

[Hydrogen electrodes were aged for 1 hour; silver–silver-chloride electrodes were aged for 12 hours.]

Temperature	Molality of potassium chloride = *m*								
	0.05	0.03	0.02	0.01	0.007	0.005	0.003	0.002	0.001
°C	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*
0	0.52725	0.53976	0.54962	0.56611	0.57459	0.58255	0.59476	0.60420	0.62059
5	.52976	.54255	.55261	.56936	.57803	.58620	.59849	.60812	.62478
10	.53229	.54532	.55550	.57263	.58144	.58963	.60222	.61210	.62908
15	.53482	.54806	.55847	.57583	.58485	.59322	.60591	.61602	.63334
20	.53738	.55085	.56143	.57915	.58828	.59678	.60968	.61994	.63760
25 [a]	.53999	.55363	.56440	.58255	.59173	.60040	.61354	.62396	.64186
25 [b]	.53998	.55364	.56435	.58257	.59174	.60042	.61356	.62393	.64190
25 [c]	.54003	.55369	.56438	.58270	.59184	.60045	.61368	.62403	.64201
30	.54250	.55644	.56738	.58566	.59514	.60394	.61731	.62789	.64618
35	.54510	.55919	.57023	.58888	.59854	.60748	.62107	.63187	.65036
40	.54752	.56190	.57318	.59206	.60187	.61096	.62475	.63571	.65457
45 [d]	.55008	.56452	.57600	.59528	.60514	.61443	.62847	.63963	.65866
45 [e]	.55011	.56455	.57606	.59529	.60519	.61454	.62853	.63972	.65875
50	.55264	.56746	.57908	.59859	.60871	.61810	.63234	.64366	.66304
55	.55519	.57023	.58207	.60184	.61210	.62164	.63610	.64767	.66729
60	.55773	.57287	.58487	.60506	.61543	.62508	.63974	.65152	.67137

[a] emf recorded 6 hours after the start of flow of the hydrogen gas.
[b] emf recorded after measurements at 0°, 5°, 10°, 15°, 20°, and 25° (first) C.
[c] emf recorded after measurements at all the other temperatures were made.
[d] emf recorded after measurements at the lower temperatures were made.
[e] emf recorded after measurements were made at 50°, 55°, and 60° C.

III. METHOD FOR THE DETERMINATION OF THE pH OF ACID POTASSIUM PHTHALATE

The relation between the emf of the cell and the hydrogen- and chloride-ion activities of the solution is given by the equation

$$E=E^\circ-(RT/F)\ln(a_Ha_{Cl})=E^\circ-(RT/F)\ln(f_Hf_{Cl}m_Hm_{Cl}), \quad (1)$$

where E is the measured emf; E° the potential of the silver–silver-chloride electrode at unit activity of hydrochloric acid; a, f, and m are, respectively, the activity, activity coefficient, and molality of the ionic species denoted by subscripts; and R, T, and F have their usual

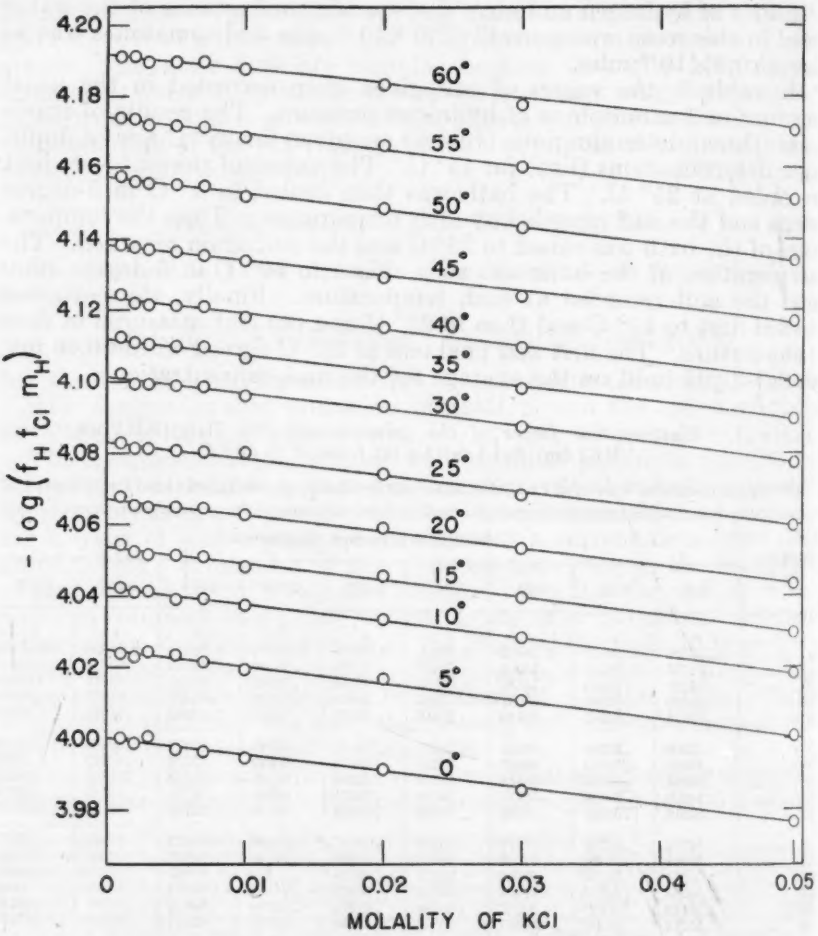

FIGURE 1.—*Plots of the numerical values of* $-\log(f_Hf_{Cl}m_H)$ *at 0° to 60° C for solutions of 0.05-m acid potassium phthalate containing different amounts of potassium chloride.*

0.09, 0.06, 0.04, 0.03, 0.02, and 0.01 were subtracted from the values at 0°, 5°, 10°, 15°, 20°, and 25° C for convenience in plotting.

significance. Upon collection of all known quantities on the left, eq 1 becomes

$$(E-E^\circ)/(RT/F)+\log m_{Cl}=-\log (f_H f_{Cl} m_H), \quad (2)$$

by which values of $-\log (f_H f_{Cl} m_H)$, a quantity proportional to pH or $-\log (f_H m_H)$, may be calculated. It would therefore be a simple matter to calculate pH values from the emf if values of $-\log f_{Cl}$ for the solution were known. Hamer and Acree [13] have shown how values of $-\log f_{Cl}$ may be determined from the emf of cells without liquid junction, using the equations of Debye and Hückel. This method entails comprehensive studies, however, of the thermodynamics of the system under study, in this case of various mixtures of *o*-phthalic acid and potassium hydroxide. However, a simpler method, although probably less precise, may be followed and is herein described for the temperature 25° C.

From the emf determinations recorded in table 1, values of $-\log (f_H f_{Cl} m_H)$ were calculated by eq 2 for each concentration of potassium chloride for the different temperatures, using the data for E° determined by Harned and Ehlers [19] and values of R, T, and F employed by Hamer, Burton, and Acree [14], and are given in table 2. These values are then plotted against the molality of potassium chloride, as shown in figure 1, and extrapolation made to zero salt concentration, which gives the value of $-\log (f_H f_{Cl} m_H)^\circ$ for 0.05-*m* acid potassium phthalate in the absence of chloride ion. The superscript, zero, is used to denote quantities for solutions containing no chloride ion. Within the experimental error (0.002 in pH unit), the values vary linearly with the molality of potassium chloride. This variation may be expressed by

$$-\log (f_H f_{Cl} m_H) = -\log (f_H f_{Cl} m_H)^\circ - k m_{KCl}, \quad (3)$$

where k is a constant whose magnitude is given by the slope of the straight lines of figure 1. Values of $-\log (f_H f_{Cl} m_H)^\circ$ and k for the different temperatures were determined by the method of least squares and are given in the last two columns of table 2. At 25° C, $-\log (f_H f_{Cl} m_H)^\circ$ equals 4.0934.

TABLE 2.—*Numerical values of* $-\log (f_H f_{Cl} m_H)$ *in 0.05-m acid potassium phthalate containing various amounts of potassium chloride from 0° to 60° C*

Temperature	Molality of potassium chloride										
	0.05	0.03	0.02	0.01	0.007	0.005	0.003	0.002	0.001	0.000	k[b]
°C											
0	4.0665	4.0755	4.0814	4.0847	4.0865	4.0871	4.0906	4.0888	4.0903	4.0903	0.48
5	4.0606	4.0706	4.0768	4.0794	4.0816	4.0836	4.0845	4.0830	4.0840	4.0851	.48
10	4.0581	4.0683	4.0735	4.0775	4.0794	4.0792	4.0815	4.0813	4.0826	4.0826	.49
15	4.0596	4.0695	4.0756	4.0782	4.0811	4.0815	4.0817	4.0825	4.0845	4.0840	.48
20	4.0633	4.0731	4.0790	4.0827	4.0848	4.0850	4.0850	4.0855	4.0880	4.0875	.48
25[a]	4.0695	4.0783	4.0843	4.0902	4.0904	4.0909	4.0913	4.0915	4.0930	4.0934	.48
30	4.0772	4.0872	4.0930	4.0960	4.0987	4.0990	4.0994	4.0995	4.1025	4.1016	.48
35	4.0894	4.0980	4.1026	4.1067	4.1098	4.1100	4.1105	4.1110	4.1125	4.1122	.46
40	4.0999	4.1095	4.1151	4.1180	4.1210	4.1213	4.1215	4.1219	4.1245	4.1237	.47
45[a]	4.1167	4.1238	4.1291	4.1340	4.1355	4.1366	4.1372	4.1379	4.1385	4.1386	.45
50	4.1338	4.1432	4.1485	4.1518	4.1548	4.1552	4.1555	4.1560	4.1575	4.1574	.47
55	4.1508	4.1600	4.1659	4.1685	4.1712	4.1717	4.1720	4.1736	4.1740	4.1741	.46
60	4.1702	4.1775	4.1830	4.1875	4.1895	4.1895	4.1895	4.1916	4.1910	4.1917	.44

[a] Only the first recorded emf were used at these temperatures. Data obtained with the second or third measurements of the emf agree with the above data within 0.0009 on the average. [b] k is the coefficient in the equation $-\log (f_H f_{Cl} m_H) = -\log (f_H f_{Cl} m_H)^\circ - k m_{KCl}$ where $-\log (f_H f_{Cl} m_H)^\circ$ represents the quantity $-\log (f_H f_{Cl} m_H)$ for zero salt concentration.

The pH value of the solution may then be obtained from this value by use of a large-scale plot of $-\log (f_H m_H)^\circ$ against $-\log (f_H f_{Cl} m_H)^\circ$ for the same ionic strength, or determined from a more sensitive plot of the differences between $-\log (f_H m_H)^\circ$ and $-\log (f_H f_{Cl} m_H)^\circ$ against $-\log (f_H f_{Cl} m_H)^\circ$. A description of the method used in the construction of the latter plot follows. Similar measurements are made with 0.05-*m* hydrochloric acid and 0.05-*m* potassium hydroxide. This alkali is used, since acid potassium phthalate is considered here; for sodium or lithium salts, sodium or lithium hydroxide would be used. From the date of Harned and Ehlers [19, 20] and of Harned and Hamer [21], values of 1.4628 and 12.7021 are obtained for $-\log (f_H f_{Cl} m_H)^\circ$ for hydrochloric acid and potassium hydroxide, respectively. Also by means of the equations

$$-\log(f_H m_H) = pH \tag{4}$$

and

$$-\log K_W/(f_{OH} m_{OH}) = -\log (f_H m_H) = pH, \tag{5}$$

the pH values of pure hydrochloric acid (eq 4) and pure potassium hydroxide (eq 5) may be calculated, where K_W is the ionization constant of water and m and f are the molalities and activity coefficients of the ions denoted by subscripts. Values of 1.3817 and 12.6114 are

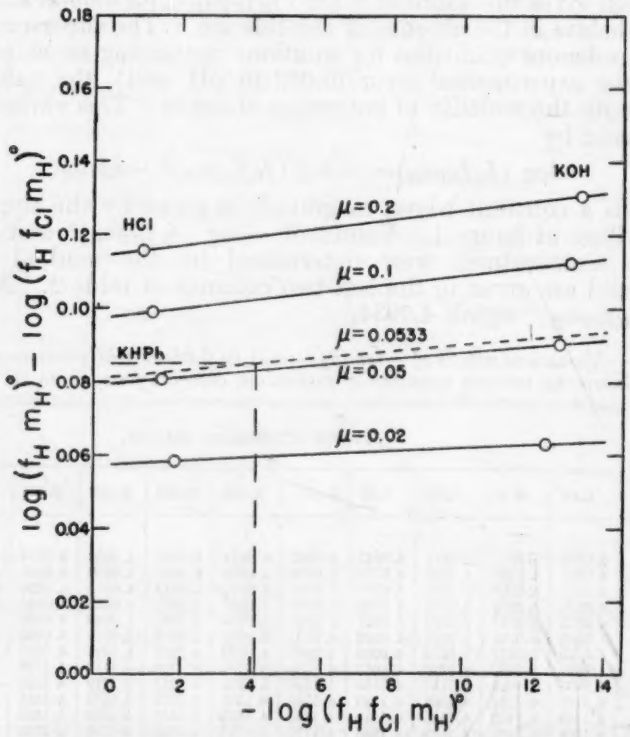

FIGURE 2.—*Plots of the differences between* $-(\log f_H m_H)^\circ$ *and* $-\log (f_H f_{Cl} m_H)^\circ$ *against* $-(\log f_H f_{Cl} m_H)^\circ$ *at 25° C for various ionic strengths of hydrochloric acid and potassium hydroxide.*

Data for acid potassium phthalate are read from these plots, as shown by the dotted vertical and horizontal lines.

obtained by these equations for the pH of 0.05-*m* solutions of hydrochloric acid and potassium hydroxide, respectively, using 0.8304 for f_H [19], 1.008×10^{-14} for K_W [21], and 0.824 for f_{OH} [22, 20].[4] Hence $-\log (f_H f_{Cl} m_H)^\circ$ and $-\log (f_H m_H)^\circ$ differ by 0.0811 for 0.05-*m* hydrochloric acid and by 0.0907 for 0.05-*m* potassium hydroxide at 25° C. If the assumption is made that a straight line may be drawn between the points located by plotting these differences against $-\log (f_H f_{Cl} m_H)^\circ$ for a definite ionic strength, it is then possible to determine the difference between $-\log (f_H f_{Cl} m_H)^\circ$ and $-\log (f_H m_H)^\circ$ for 0.05-*m* acid potassium phthalate from the plot.[5]

In figure 2 these differences are shown plotted against values of $-\log (f_H f_{Cl} m_H)^\circ$ for ionic strengths of 0.02, 0.05, 0.10, and 0.20 calculated in a similar manner from data in the literature [19 to 22] for 25° C. From the plot, a difference of 0.0831 is read for 0.05-*m* acid potassium phthalate, for which $-\log (f_H f_{Cl} m_H)^\circ$ is 4.0934; hence its pH value is 4.0934—0.0831, or 4.010 at 25° C.

However, the ionic strength of 0.05-*m* acid potassium phthalate is somewhat larger than 0.05, owing to several ionic reactions which occur in an aqueous solution of this salt. When acid potassium phthalate is dissolved in water it ionizes according to the equation

$$KHPh \rightarrow K^+ + HPh^-, \tag{6}$$

and since HPh^- behaves as an acid, it ionizes further:

$$HPh^- \rightleftharpoons H^+ + Ph^=, \tag{7}$$

to give a certain amount of the bivalent phthalate ion. However, H^+ does not equal $Ph^=$, since part of the H^+ ions reacts with HPh^- according to the reaction

$$H^+ + HPh^- \rightleftharpoons H_2Ph, \tag{8}$$

to give a definite amount of undissociated *o*-phthalic acid, H_2Ph. The amounts of H_2Ph, HPh^-, and $Ph^=$ may be calculated by using the mass action equations for the above reactions and for the two steps in the ionization of *o*-phthalic acid with the aid of the Debye-Hückel equations for the activity coefficients. These were found to be, respectively, 0.0032, 0.0436, and 0.0032, using 0.0013 and 0.0000038, respectively, [23] for K_1 and K_2, the first and second ionization constants of *o*-phthalic acid. Therefore, the ionic strength of a 0.05-*m* solution of acid potassium phthalate is 0.0533 instead[6] of 0.05. In figure 2, the dotted line corresponds to this ionic strength. The position of the dotted line was determined from that of the others by means of plots of $[\log (f_H m_H)^\circ - \log (f_H f_{Cl} m_H)^\circ]$ for pH values of 0 and 14 against the ionic strength. A difference of 0.0854 is then read from this line for acid potassium phthalate, and hence its pH value is 4.0934—0.0854, or 4.008, which is only 0.002 pH unit lower than the value based upon the stoichiometric ionic strength and is the value certified by this Bureau for acid potassium phthalate Standard Sample 84a.

[4] The assumption is made that for $f_{OH} = \sqrt{f_K f_{OH}}$ for the alkaline solutions and $f_H = \sqrt{f_H f_{Cl}}$ for the acid solutions, or that the activity coefficient of an ion in an electrolyte is equal to the mean activity coefficient of the ions composing the electrolyte. This does not imply that $f_H = f_K = f_{Cl} = f_{OH}$. See E. A. Guggenheim, J. Phys. Chem. **34**, 1758 (1930) for a discussion of this assumption.

[5] The small contribution of m_H to the ionic strength can be calculated from the provisional values of pH.

[6] The ionic strength is equal to $1/2\ \Sigma_i m_i z_i^2$, where m_i and z_i represent the molality and valence of each ionic species. For the above case the ionic strength equals $m_{HPh} + 3m_{Ph} + 1/2 m_H$ or $(0.0436 + 0.0096 + 0.00005 = 0.05325)$.

This method is estimated to be accurate within 0.005 to 0.01 pH unit, even if the stoichiometric ionic strength is employed instead of the true ionic strength.[7] The pH values based upon an ionic strength of 0.05 and of 0.0533 are given in columns 3 and 4 of table 3 for the temperatures[8] 0° to 60° C. Data obtained by former investigators by other methods [1 to 4] are given for comparison. The values obtained in this investigation are 0.04 to 0.05 unit higher than those of Clark and Lubs [1] and Kolthoff and Tekelenburg [2], who used the concentration instead of the activity of hydrogen ions as a basis for their pH scale, but are in close agreement with the values of Hitchcock and Taylor [3] and of MacInnes, Belcher, and Shedlovsky [4].

TABLE 3.—*pH values of 0.05–m acid potassium phthalate at temperatures from 0° to 60° C, inclusive*

[Data of other investigators are given for comparison]

Temperature	$-\log(f_H f_{Cl} m_H)^\circ$	pH (based on an ionic strenght of 0.05)[a]	pH (based on an ionic strength of 0.0533)[a]	Clark and Lubs (1916) [1]	Kolthoff and Tekelenburg (1927) [2]	Hitchcock and Taylor (1937–38) [3]	MacInnes, Belcher, and Shedlovsky (1938) [4]
°C							
0	4.0903	4.009	4.007	----	----	----	----
5	4.0851	4.004	4.002	----	----	----	----
10	4.0826	4.001	3.999	----	----	----	----
12.5	----	----	[b] 4.000	----	----	----	4.000
15	4.0840	4.002	4.000	----	----	----	----
18	----	----	[b] 4.001	----	[c] 3.94 (3.92)	----	----
20	4.0875	4.005	4.003	3.974	----	----	----
25	4.0934	4.010	4.008	----	----	4.008	4.000
30	4.1016	4.018	4.016	----	3.96 (3.92)	----	----
35	4.1122	4.027	4.025	----	----	----	----
38	----	----	[b] 4.032	----	----	4.025	4.015
40	4.1237	4.038	4.036	----	3.99 (3.93)	----	----
45	4.1386	4.052	4.050	----	----	----	----
50	4.1574	4.070	4.068	----	4.02 (3.94)	----	----
55	4.1741	4.086	4.084	----	----	----	----
60	4.1917	4.102	4.101	----	4.05 (3.94)	----	----

[a] pH values were calculated by the equation $\mathrm{pH}=\frac{-(\log f_H f_{Cl} m_H)^\circ - P}{Q}$.

[b] Values calculated by equation 13.

[c] Values in parentheses were determined with a hydrogen electrode, whereas the other values of Kolthoff and Tekelenburg were determined with a quinhydrone electrode. They considered the hydrogen-electrode values less reliable because of possible reduction of the acid potassium phthalate.

The straight lines of figure 2 may be expressed by the equation

$$\log (f_H m_H)^\circ - \log (f_H f_{Cl} m_H)^\circ = a - b \log (f_H f_{Cl} m_H)^\circ, \qquad (9)$$

where a is the value of $\log (f_H m_H)^\circ - \log (f_H f_{Cl} m_H)^\circ$ for $-\log (f_H f_{Cl} m_H)^\circ = 0$, and b is a constant whose magnitude at various ionic strengths is given by the slopes of the straight lines. This equation may be converted to the form

$$\mathrm{pH} = [-\log (f_H f_{Cl} m_H)^\circ - P]/Q, \qquad (10)$$

[7] It is difficult at the present time to give an evaluation of the accuracy of this method. Further work on the thermodynamics of mixtures of o-phthalic acid and potassium hydroxide (publication pending) will shed light on this subject. However, the close agreement of the pH value for 0.05-*m* acid potassium phthalate at 25° C obtained by this method with the values obtained by Hitchcock and Taylor and by MacInnes, Belcher, and Shedlovsky given in table 3 indicates that this method is probably accurate within 0.005 to 0.01 pH unit.

[8] Harned and Cook [11] obtained activity coefficients at only 0°, 10°, 20°, 25°, and 35° C. Values at the other temperatures were obtained by extrapolation.

where P and Q are new constants. Values of P and Q for ionic strengths of 0.05 and 0.0533 are given in table 4 for temperatures from 0° to 60° C, inclusive. Values of P and Q for different ionic strengths at 25° C are given in table 5. Furthermore, since $-\log (f_H f_{Cl} m_H)$ equals $(E-E^\circ)/(RT/F)+\log m_{Cl}$, eq 10 may be written

$$pH=[(E-E^\circ)/(RT/F)+\log m_{Cl}-P]/Q, \quad (11)$$

by which the pH may be calculated directly from the emf and the numerical values of P and Q given in table 4, remembering that P and Q depend upon the ionic strength and are for solutions containing no chloride ion. For solutions containing Cl^- ions, different values of P and Q must be used, which are given in table 6.

TABLE 4.—*Numerical values of the constants P and Q of equation 10 for ionic strengths of 0.05 and 0.0533*

Temperature	Ionic strength			
	0.05		0.0533	
°C	P	Q	P	Q
0	0.0772	1.00107	0.0787	1.00112
5	.0773	1.00102	.0789	1.00106
10	.0776	1.00096	.0795	1.00101
15	.0782	1.00094	.0799	1.00098
20	.0789	1.00090	.0805	1.00094
25	.0796	1.00085	.0814	1.00089
30	.0807	1.00082	.0824	1.00086
35	.0818	1.00079	.0835	1.00083
40	.0829	1.00076	.0847	1.00080
45	.0838	1.00073	.0856	1.00076
50	.0849	1.00068	.0867	1.00072
55	.0859	1.00066	.0877	1.00070
60	.0869	1.00065	.0888	1.00067

TABLE 5.—*Numerical values of the constants P and Q of equation 10 for different ionic strengths at 25° C*

Ionic strength	P	Q
0.005	0.0313	1.00040
.01	.0423	1.00055
.02	.0575	1.00068
.05	.0796	1.00085
.10	.0976	1.00092
.20	.1146	1.00096

The pH values of the solutions of 0.05-*m* acid potassium phthalate containing various amounts of potassium chloride were calculated similarly, using the proper values of P and Q. The values are given in table 7, and in figure 3 are shown plotted against the molality of potassium chloride for temperatures of 0°, 25°, 45°, and 60° C. The plots exhibit a slight curvature, appearing at molalities between 0.03 and 0.04. The variation of pH with salt concentration may be expressed at all the temperatures by the equation

$$pH_{\text{with salt}}=pH_{\text{without salt}}-0.993m_{KCl}+2.124m^2_{KCl}. \quad (12)$$

In figure 4 the pH of 0.05-*m* acid potassium phthalate (curve A) and of 0.05-*m* acid potassium phthalate containing 0.02-*m* potassium chloride (curve B) and 0.05-*m* potassium chloride (curve C) are shown plotted against the temperature in degrees centigrade. The curves

TABLE 6.—*Numerical values of constants P and Q for various concentrations of potassium chloride in 0.05-m acid potassium phthalate for use in equation 10*

Temperature	Molality of potassium chloride								
	0.001	0.002	0.003	0.005	0.007	0.01	0.02	0.03	0.05
	P VALUES								
°C									
0	0.0783	0.0788	0.0794	0.0805	0.0811	0.0830	0.0872	0.0916	0.0980
5	.0791	.0796	.0804	.0814	.0820	.0838	.0880	.0926	.0988
10	.0799	.0804	.0810	.0822	.0829	.0847	.0890	.0936	.0999
15	.0807	.0813	.0819	.0829	.0837	.0856	.0899	.0946	.1009
20	.0810	.0821	.0827	.0839	.0845	.0864	.0909	.0956	.1010
25	.0824	.0830	.0836	.0848	.0855	.0874	.0919	.0965	.1029
30	.0833	.0836	.0841	.0857	.0865	.0883	.0928	.0975	.1042
35	.0842	.0847	.0853	.0866	.0874	.0892	.0938	.0985	.1052
40	.0851	.0857	.0864	.0875	.0883	.0903	.0948	.0996	.1065
45	.0861	.0867	.0873	.0885	.0894	.0913	.0959	.1008	.1076
50	.0871	.0877	.0884	.0896	.0904	.0924	.0971	.1020	.1090
55	.0881	.0887	.0894	.0906	.0915	.0935	.0981	.1032	.1101
60	.0891	.0898	.0904	.0917	.0926	.0946	.0994	.1044	.1114
	Q VALUES								
0	1.00111	1.00110	1.00110	1.00109	1.00109	1.00108	1.00103	1.00097	1.00089
5	1.00105	1.00104	1.00104	1.00103	1.00103	1.00102	1.00097	1.00091	1.00082
10	1.00100	1.00099	1.00099	1.00097	1.00097	1.00096	1.00091	1.00084	1.00075
15	1.00097	1.00096	1.00096	1.00094	1.00093	1.00091	1.00085	1.00078	1.00068
20	1.00093	1.00092	1.00092	1.00090	1.00089	1.00087	1.00081	1.00073	1.00063
25	1.00088	1.00087	1.00087	1.00084	1.00084	1.00082	1.00076	1.00068	1.00058
30	1.00085	1.00084	1.00084	1.00082	1.00081	1.00079	1.00073	1.00065	1.00055
35	1.00082	1.00081	1.00081	1.00079	1.00078	1.00076	1.00070	1.00062	1.00052
40	1.00079	1.00078	1.00078	1.00076	1.00075	1.00073	1.00067	1.00059	1.00045
45	1.00075	1.00074	1.00073	1.00071	1.00069	1.00067	1.00061	1.00053	1.00043
50	1.00071	1.00069	1.00068	1.00066	1.00064	1.00062	1.00055	1.00046	1.00035
55	1.00069	1.00067	1.00066	1.00064	1.00062	1.00060	1.00053	1.00044	1.00033
60	1.00066	1.00064	1.00063	1.00061	1.00059	1.00057	1.00050	1.00041	1.00030

TABLE 7.—pH *values of 0.05-m acid potassium phthalate containing various amounts of potassium chloride at temperatures from 0° to 60° C, inclusive*

Temperature	Molality of potassium chloride								
	0.001	0.002	0.003	0.005	0.007	0.01	0.02	0.03	0.05
°C									
0	4.008	4.006	4.007	4.002	4.001	3.997	3.990	3.980	3.965
5	4.001	3.999	4.000	3.998	3.996	3.992	3.985	3.974	3.959
10	3.999	3.997	3.997	3.993	3.993	3.989	3.981	3.971	3.955
15	4.000	3.997	3.996	3.995	3.994	3.989	3.982	3.972	3.956
20	4.003	4.000	3.999	3.998	3.997	3.993	3.985	3.975	3.960
25	4.007	4.005	4.004	4.003	4.002	4.000	3.989	3.979	3.964
30	4.016	4.012	4.012	4.010	4.009	4.005	3.997	3.987	3.971
35	4.025	4.023	4.022	4.020	4.019	4.014	4.006	3.997	3.982
40	4.036	4.033	4.032	4.031	4.030	4.025	4.018	4.008	3.992
45	4.049	4.048	4.047	4.045	4.043	4.040	4.031	4.021	4.008
50	4.068	4.066	4.064	4.063	4.062	4.057	4.049	4.039	4.024
55	4.083	4.082	4.080	4.079	4.077	4.073	4.066	4.055	4.040
60	4.099	4.099	4.097	4.095	4.095	4.091	4.082	4.072	4.058

are displaced a constant amount at all temperatures by the addition of potassium chloride and exhibit a minimum at about 10° C. The variation of the pH of a 0.05-*m* solution of acid potassium phthalate containing no potassium chloride may be represented by the equation

$$\text{pH}=5.13 \log T+1519.62/T+0.01092T-17.039 \qquad (13)$$

where $T=t°\text{C}+273.16$. For the solutions containing salt, the equation is modified by changing 17.039 by an amount determined by eq 12. The pH values are constant within 0.005 pH unit between 0° and 30° C, and this fact increases their usefulness as pH standards.

The potentiometric method herein described is a general one, in that it may be used equally well for other concentrations and other buffer solutions for the temperature range of 0° to 60° C. It has the advantage of being less involved, although less precise, than ones based upon a complete thermodynamic study of the system, and the pH value of a solution may be determined directly from the electromotive force of galvanic cells without liquid junction.

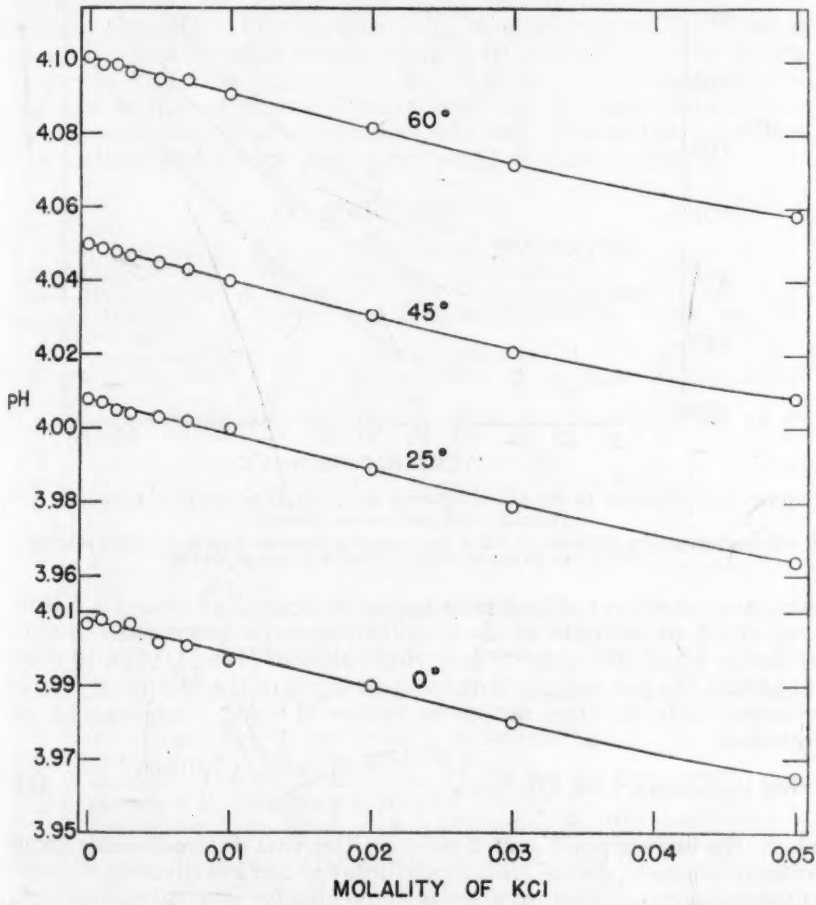

FIGURE 3.—*Variation in the* pH *of 0.05-m acid potassium phthalate with the molality of added potassium chloride at 0°, 25°, 45°, and 60° C.*

The method may also be used to determine approximately the pH values and ionic strengths of unknowns [24] of low salt content, but if chloride salts are present, the chloride concentration must be determined for use in the equations. The computations are simpler if the unknown contains no chloride. First, two different amounts of potassium chloride are added to two separate portions of the unknown, and $-\log (f_H f_{Cl} m_H)$ is calculated by eq 2 for each portion from the electromotive force and the known chloride-ion concentration. The value of $-\log (f_H f_{Cl} m_H)^\circ$ for the solution without added chloride is then obtained by means of a straight-line plot of the values of $-\log (f_H f_{Cl} m_H)$ against the chloride-ion concentration. This value is

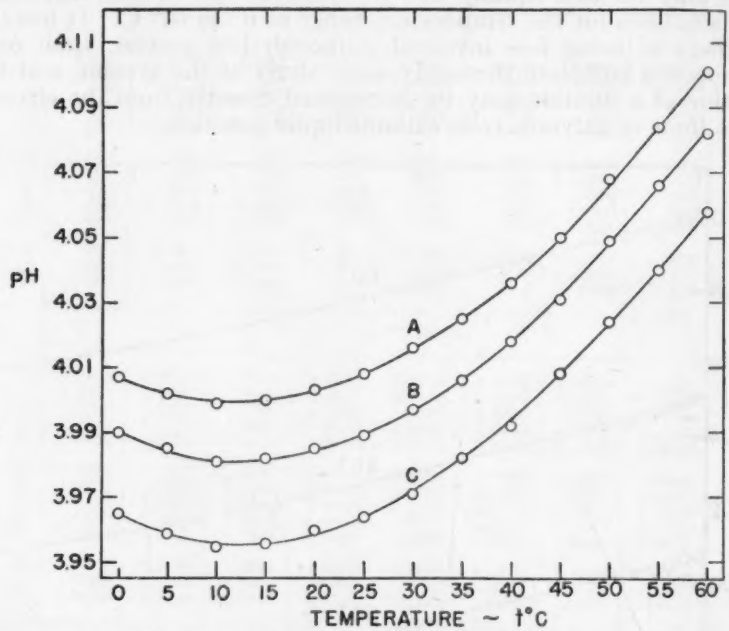

FIGURE 4.—*Variation in the* pH *of aqueous solutions of mixtures of acid potassium phthalate and potassium chloride.*

A, 0.05-*m* acid potassium phthalate; *B*, 0.05-*m* acid potassium phthalate +0.02-*m* potassium chloride; *C*, 0.05-*m* acid potassium phthalate +0.05-*m* potassium chloride.

then converted into pH units by means of figure 2 or by eq 10. However, the ionic strength of the unknown must be determined in order to decide which line of figure 2 or what values of P and Q of eq 10 to use to obtain the pH value. The ionic strength of the unknown may be obtained from the two measured values of $-\log (f_H f_{Cl} m_H)$ by the equation

$$-\log (f_H f_{Cl} m_H)_1 + \log (f_H f_{Cl} m_H)_2 = \frac{1.0196\sqrt{x}+c_1}{1+\sqrt{x}+c_1} - \frac{1.0196\sqrt{x}+c_2}{1+\sqrt{x}+c_2}, \quad (14)$$

where the subscripts 1 and 2 refer to the two different chloride-ion concentrations (c_1 and c_2) that were employed and x is the ionic strength of the unknown. This equation is applicable for ionic strengths of 0.2 or less. An illustration of the method follows.

An unknown solution [9] upon the addition of 0.01–*m* and 0.02–*m*

[9] This solution contained 0.01 mole of acid potassium phthalate and 0.01 mole of dipotassium phthalate per 1,000 g of water.

potassium chloride gave, respectively, electromotive forces of 0.65431 v and 0.63472 v. These give, respectively, 5.3035 and 5.2743 for $-\log (f_H f_{Cl} m_H)$. The difference (0.02922) of the two values added to the first value gives 5.3327 for $-\log (f_H f_{Cl} m_H)^\circ$ for the unknown solution containing no chloride ion. The same difference substituted in eq 14 gives 0.0037 for x, the ionic strength of the unknown. From interpolation of the data of table 4, P and Q are, respectively, 0.0200 and 1.00025. Therefore, by means of eq 10 the pH of the unknown is $(5.3327-0.0200)/1.00025=5.311$. This solution was known to have an ionic strength of 0.004 and a pH of 5.326, which agree adequately with the calculated values.

Similar applications to other unknowns may not be as successful. However, the method may be employed with a precision of about 0.1 or better in pH for solutions of ionic strength less than 0.2. The values of P given in table 5 correspond to the errors in pH at different ionic strengths if no corrections were made for the ionic strength. For example, in the above illustration the error in the pH of the unknown solution would be 0.02 if no corrections had been made for the ionic strength. Furthermore, the method cannot be applied successfully to a chloride solution unless its concentration is known because the emf is a function of the activity of the chloride ion. Additional studies of effects of polar and nonpolar salts of high concentrations on the pH of solutions should make possible an extension of the method and theory to a wider range of ionic strengths.

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THERMAL PROPERTIES OF MOIST FABRICS

By Charles W. Hock, Arnold M. Sookne, and Milton Harris [1]

ABSTRACT

The "chilling effect", or "clamminess", that moist fabrics produce when in contact with the body was evaluated by subjective tests, by measurement of the drop in temperature that ensued when the moist fabrics were placed on an artificial "skin" surface, and by tests with a moisture-sensitive paper designed to measure the extent of contact which the fabrics made with a surface. Using fabrics of various fiber compositions and constructions, a good qualitative relation was found in these tests. Fabrics which produced considerable chilling in subjective tests were found to make good contact and to cause a substantial drop in skin temperature. Conversely, fabrics which caused little or no clamminess made poor contact and the accompanying drop in temperature was relatively small. The results of these experiments show clearly the progressive improvement of the fabrics with respect to chilling, as their wool content is increased, and also the superiority of certain types of construction that minimize the extent of contact of the fabrics with the skin.

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I. INTRODUCTION

Practical experience has demonstrated that moist fabrics in contact with the body produce an unpleasant sensation, commonly referred to as a "chilling effect" or a "clammy feel." The intensity of the sensation varies with different fibers and fabrics; thus, on the basis of general experience, the merits of wool fabrics over similar cotton fabrics have long been recognized. This is one of the reasons, for example, for the preference usually given to woolen underwear and other garments for use in cold climates under conditions where physical labor causes considerable perspiration. It also accounts for the preference commonly expressed for woolen bathing suits.

In selecting fabrics for warmth, the thermal resistance is a factor of primary importance, and this property has been measured by

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

many investigators [1, 2, 3, 4, 5, 6].[2] In general, the results indicate that for comparable thicknesses and densities there are no outstanding differences between different fabrics. The chilling effect noted above, however, has suggested that marked differences may be obtained as the amount of moisture contained in a fabric is increased, and accordingly an investigation was undertaken to evaluate this and other factors contributing to the phenomenon of chilliness, or clamminess, in wet fabrics.

II. MATERIALS

Thirty-six samples of knit underwear fabric, prepared especially for experimental purposes, were used throughout the investigation. The fabrics consisted of plain and special knits of various weights and thicknesses and of different fiber compositions, as described in tables 1 and 2. Both unlaundered and twice-laundered samples were examined.

TABLE 1.—*Description of fabrics*

Sample	Type of spinning	Type of knitting	Fiber content of yarn	Nominal weight of undershirts (1 dozen, size 40) unlaundered
				lb
A	Cotton	Rib	100% cotton	10½
B	do	do	75% cotton, 25% wool	10½
C	French	do	50% cotton, 50% wool	10½
D	do	do	do	10½
E	do	do	25% cotton, 75% wool	10½
F	do	do	100% wool	10½
G	Cotton	do	100% cotton	8 to 8¼
H	do	do	75% cotton, 25% wool	8 to 8¼
I	French	do	50% cotton, 50% wool	8 to 8¼
K	do	do	25% cotton, 75% wool	8 to 8¼
L	do	do	100% wool	8 to 8¼
M	Cotton	do	100% cotton	5½ to 6
N	do	do	75% cotton, 25% wool	5½ to 6
O	French	do	50% cotton, 50% wool	5½ to 6
Q	do	do	25% cotton, 75% wool	5½ to 6
R	do	do	100% wool	5½ to 6
CA	do	Mesh stitch	50% cotton, 50% wool	8 to 8¼
CB	do	do	do	5½ to 6
CC	do	Waffle stitch	do	10½
CD	Filament	Rib	100% acetate filament	Light[a]
CE	do	do	100% viscose-rayon filament	Do.
CF	do	do	100% nylon filament	Do.
FC	French	Flat	50% cotton, 50% wool	10½
FI	do	do	do	8 to 8¼
FM	Cotton	do	100% cotton	5½ to 6
FO	French	do	50% cotton, 50% wool	5½ to 6
XA	do	Shaker stitch	do	10½
XB	Cotton and French	Duofold type	100% cotton in, 100% wool out	10½
XC	do	do	100% cotton out, 100% wool in	10½
XD	French	Interlock	50% cotton, 50% wool	8 to 8¼
XE	do	Terry stitch	do	10½
XF	Cotton	Alternate rib feed	75% cotton, 25% wool	10½
XG	do	Rib	50% cotton, 50% wool	8 to 8¼
XH	do	Flat fleece lined	100% cotton	10½
XI	Woolen	Rib	100% wool	10½
XJ	Cotton	Raschel	100% cotton	10½

[a] The nominal weights of these fabrics in pounds per dozen undershirts of size 40 was not given. Their actual weights in ounces per square yard are as follows: *CD*, 3.4; *CE*, 4.2; *CF*, 5.4

[2] Figures in brackets indicate the literature references at the end of the paper.

TABLE 2.—*Properties of twice-laundered fabrics*

Sample	Weight of fabrics	Thickness of fabrics at pressure of 0.1 lb/in.²	Air permeability [a] at pressure drop of 0.5 in. H_2O	Thermal [b] transmission
	oz/yd²	*in.*	*ft³/(min×ft²)*	*Btu/(° F×hr×ft²)*
A	11.4	0.063	86	1.24
B	12.3	.073	82	1.24
C	12.0	.078	85	1.20
D	10.8	.066	126	1.25
E	11.7	.070	137	1.24
F	9.8	.076	197	1.18
G	9.8	.061	101	1.30
H	9.7	.072	109	1.20
I	10.9	.077	94	1.20
K	9.5	.073	195	1.26
L	9.9	.067	215	1.20
M	6.0	.048	180	1.33
N	6.3	.055	193	1.26
O	6.2	.054	239	1.25
Q	6.4	.057	208	1.24
R	7.0	.080	310	1.15
CA	8.3	.068	238	1.32
CB	4.9	.055	390	1.32
CC	13.0	.108	144	1.23
CD	3.6	.023	[c] 249	1.48
CE	4.2	.028	[c] 242	1.48
CF	5.5	.032	[c] 106	1.42
FC	9.1	.060	102	1.26
FI	6.9	.044	195	1.33
FM	5.7	.045	189	1.34
FO	5.4	.040	256	1.33
XA	9.9	.070	164	1.22
XB	10.7	.095	178	1.16
XC	10.9	.091	162	[d] 1.07
XD	10.4	.072	99	1.24
XE	10.4	.097	116	1.12
XF	10.7	.077	106	1.24
XG	9.8	.074	121	1.29
XH	8.9	.115	81	1.04
XI	9.0	.089	204	1.18
XJ	8.2	.075	504	1.31

[a] Measured with the instrument described by Schiefer and Boyland [7].
[b] Measured with the instrument described by Cleveland [8].
[c] The values for the air permeability of samples *CD*, *CE*, and *CF* are for a pressure difference across the fabric of 0.05 inch of water, not 0.5 inch as used for all other samples. The air permeability of these samples was too high to measure at 0.5-inch pressure difference.
[d] With sample *XC*, a duofold fabric, the test was first carried out with the wool layer inside (i. e., against the heating plate of the apparatus) and then with the cotton layer inside. The results were 1.07 and 1.14, respectively.

III. EXPERIMENTAL PROCEDURE

1. SUBJECTIVE TESTS

These tests were carried out in a room conditioned at 21.1° C and 65-percent relative humidity. Samples of the fabrics, 3½ inches square, were soaked in water at the temperature of the conditioning room, and then dried in a towel until they contained the desired amount of water. The fabrics were tested when containing 100, 150, and 200 percent of moisture, based on their conditioned weights. All the fabrics were used in subjective tests, although each fabric was not tested with every other fabric because of the large number of tests that would be required. They were tested two at a time, on five male subjects, by simultaneously placing one fabric on the right and the other on the

left arm (radial ulnar region of the forearm). The subject was than asked whether he detected a difference in chilling effect between the two arms, and if so, which fabric gave the greater sensation of chilling. Each fabric was left on the arm for 15 seconds, and then removed, because it was found that the subject's immediate reaction appeared to be most reliable. Although some persons were able to perceive slight differences better than others, the subjective reactions of various individuals were in very good agreement.

2. MEASUREMENT OF DROP IN SURFACE TEMPERATURE

The apparatus used to determine the drop in surface temperature was essentially a constant-temperature oil bath (fig. 1). In order to provide conditions under which a substantial drop in "skin" temperature could be measured, the heated surface was covered with several layers of asbestos sheeting and a layer of waterproof rubberized cloth, the total thickness of this cover being approximately $\frac{3}{16}$ inch. The skin temperature was measured by four copper-constantan thermocouples, symmetrically placed on the outerside of the rubberized cloth, and held in position by a thin layer of cellulose nitrate cement. The thermocouples were connected in series, and the ice point (0° C) was

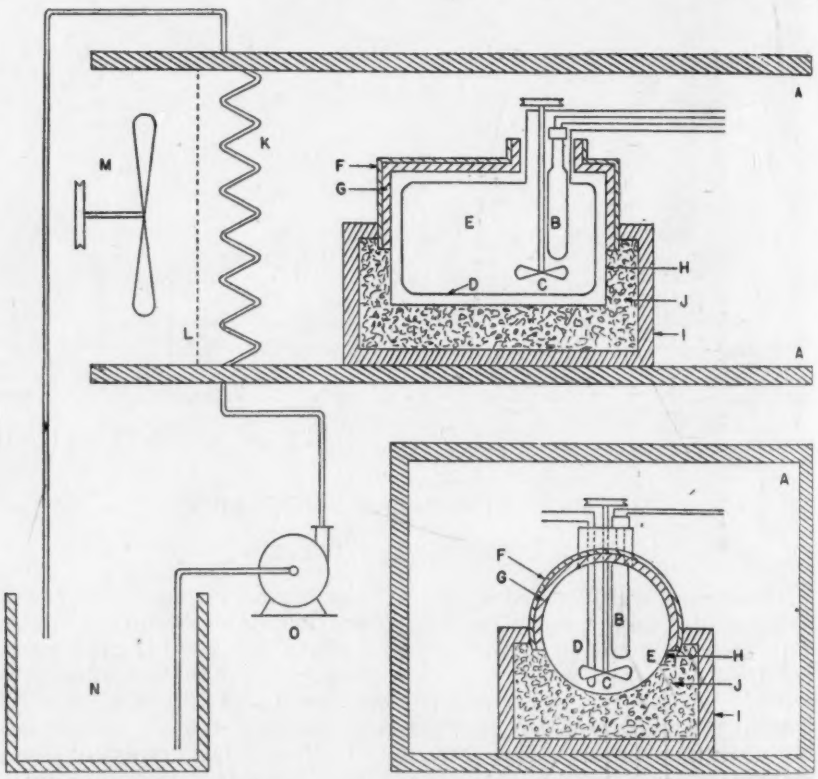


FIGURE 1.—*Diagram of apparatus for measuring drop in "skin" temperature.*

Upper and left portions, schematic side view; lower right, cross section. *A*, Outer box; *B*, thermoregulator; *C*, mechanical stirrer; *D*, heater; *E*, oil; *F*, rubberized fabric; *G*, asbestos; *H*, metal container; *I*, wooden box; *J*, insulation; *K*, radiator; *L*, cheesecloth; *M*, fan; *N*, water tank; and *O*, pump.

used as the reference temperature. A switch arrangement made it possible to measure with a potentiometer each individual electromotive force, as well as the sum of the four individual values. The average skin temperature was calculated from one-fourth of the value of the potential difference of the four units in series. To insure a highly constant skin temperature, the heating apparatus was placed in a small conditioning cabinet, which in turn was placed in a room maintained at 21.1° C and 65-percent relative humidity. Water at room temperature is circulated through the radiator, K; the fan, M, blows air at room temperature first over the radiator and then over the heating apparatus. Since the water in the radiator does not respond to the relatively short-period temperature fluctuations of the air in the room, the temperature within the cabinet is considerably more constant than that in the room. Using this device, the average temperature of the "skin" surface was constant to $\pm 0.1°$ C. The internal temperature of the bath was held at $50.0° \pm 0.05°$ C, and the average corresponding skin temperature was 37.5° C.[3]

The experimental procedure consisted in first measuring the skin temperature when the apparatus, without a test fabric on it, was in equilibrium with its surroundings. Subsequently, a moist fabric was placed on the apparatus. The moist fabrics were prepared by soaking approximately 3.5- by 6-inch samples in distilled water, the temperature of which was the same as that of the conditioning room, and then pressing the samples gently between towels until they contained 150 percent of moisture, based on the weight of the conditioned cloth. The moist fabric was placed on the apparatus so as to cover the thermocouples, and was covered immediately with a cheesecloth belt (approximately 4 in. wide) weighted at both ends (0.3 lb per end) in order to hold the sample in close contact with the heated surface. The change in surface temperature was followed as a function of time, the first reading being made 30 seconds after the initial contact of the moist fabric with the heated surface. Observations were made for 10 minutes and then discontinued, because it was found that further changes in temperature occurred only very slowly.

3. "CONTACT" TESTS

Since it is reasonable to expect that the chilling effect of wet fabrics may be related to the extent of contact which they make with the skin, a method was devised to check this hypothesis. A moisture-sensitive paper was prepared by impregnating a soft paper [4] with a water-soluble dye of high tinctorial power,[5] according to the following procedure. A mixture consisting of 5 g of dye, 30 g of crude milled rubber, and 1 liter of Stoddard's solvent was prepared by first dissolving the rubber in the solvent, and then grinding together the dye and rubber solution in a mortar. To insure uniformity of distribution, the mixture was subsequently placed on a mechanical shaker for half an hour. The dye is insoluble in the organic solvent and does not appear red under these conditions; the rubber aids in dis-

[3] Since a setup that would discriminate between fabrics with fairly similar thermal properties was required, the drop in skin temperature was accentuated by using a relatively hot skin (37.5° C) and a thick layer of insulation. The good correlation of these measurements with subjective tests demonstrates the validity of this procedure for the purpose of evaluating the fabrics.

[4] The paper was a soft sheet made from wood pulp (No. 1 alpha), containing a small amount of rosin size (sizing value by the dry indicator method: 28 sec), basis weight 23 to 24 lb, 17 by 22 in.—500 sheets.

[5] The dye was basic fuchsine (du Pont fuchsine concentrated powder, L7596).

persing the dye and imparts to the finished paper certain desirable properties. Strips of the paper were dipped in the impregnating mixture and hung up to dry at room temperature. The last traces of solvent were removed from the papers by placing them in a vacuum oven at 65° C for 15 to 20 minutes. After trimming the papers to the desired size, they were ready for use.

The test for contact was carried out by placing pieces of the wet fabrics, 3½ inches square, on the papers for 10 minutes, under a pressure of 0.5 lb per square inch. A piece of the sensitized paper was first laid on a dry glass surface. The wet fabric was then placed on top of the paper, and covered with a glass square of similar size, and weights to bring the pressure to the stated amount. After 10 minutes the fabrics and weights were removed. The papers, which were practically colorless originally, became red where the moist fabrics touched them, thereby indicating the extent of contact of the fabrics.[6] Photometric measurements of the reflectance of the papers were subsequently made, thus making it possible to assign to each fabric a numerical value indicative of its contact at any given moisture content. The measurements were made by means of a Martens photometer with a filter to isolate the 560-millimicron line.

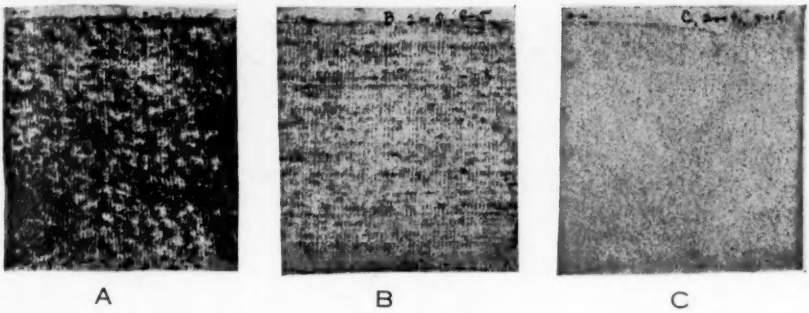
IV. RESULTS AND DISCUSSION

1. QUALITATIVE RELATION BETWEEN SUBJECTIVE AND OBJECTIVE TESTS

This investigation was undertaken not to develop a standard technique for evaluating the chilling properties of fabrics, but rather to develop a method for studying a phenomenon which has been observed empirically for a long time. Owing to the many complex factors which contribute to this phenomenon, an attempt will not be made to present the data on a quantitative basis. It is recognized, furthermore, that only one aspect of the larger problem of the thermal properties of fabrics has been studied. Nevertheless, several significant relationships were noted, and these will be discussed in more or less general terms, making no effort to account for small differences between the many and diverse fabrics included in the investigation.

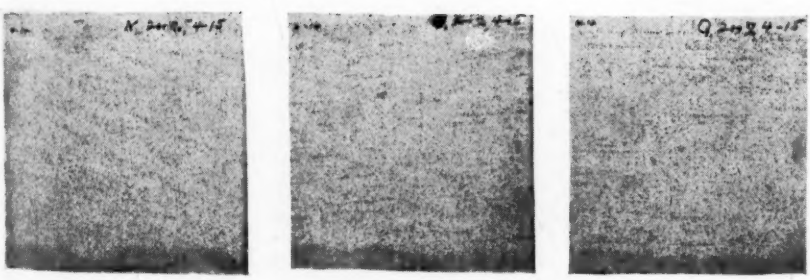
The results of the subjective tests were in very good agreement with the direct measurements of drop in temperature and degree of contact. The results of a typical set of subjective experiments are given in table 3, and may be compared with the corresponding objective measurements of figures 2 to 21. When, as, for example, with sample *A*, the subject experienced pronounced chilling, a substantial drop in temperature was measured, and the fabric was found to make good contact with the skin. On the other hand, a smaller drop in temperature was measured, and poor contact was observed in fabrics such as sample *F*, which did not produce a sensation of chilling to the subject. This correlation between subjective reaction and contact was especially interesting when the fabrics were placed on the moisture-sensitive papers immediately after their removal from the arm. Invariably, when the subjects experienced pronounced differences in comfort, similar outstanding differences in contact were observed. Likewise,

[6] This test does not actually measure the contact which the fabrics make with the human skin, but for the purposes of the present investigation, the test is believed to be an adequate indirect measure of this property.



A B C

G H I



N O Q

FIGURE 2.—*"Contact" impressions obtained with fabrics containing 200 percent of moisture.*

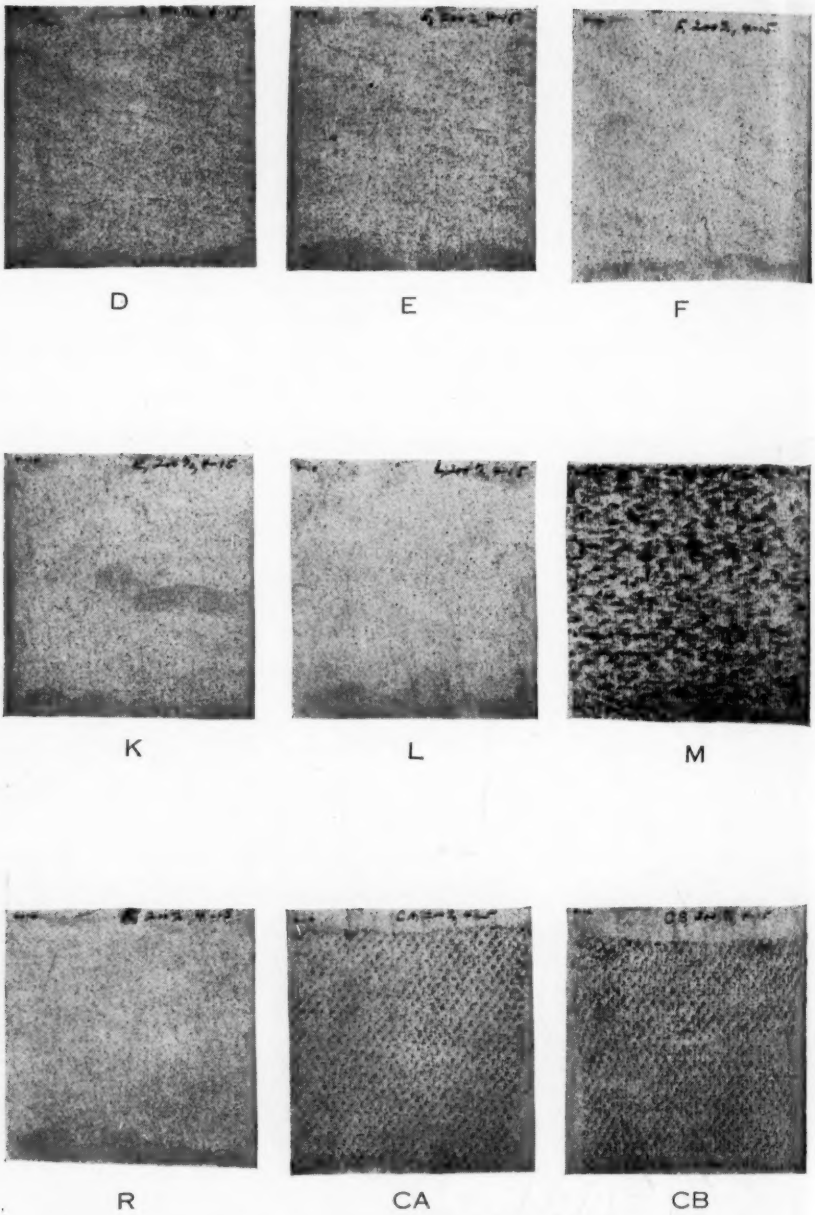


FIGURE 3.—*"Contact" impressions obtained with fabrics containing 200 percent of moisture.*

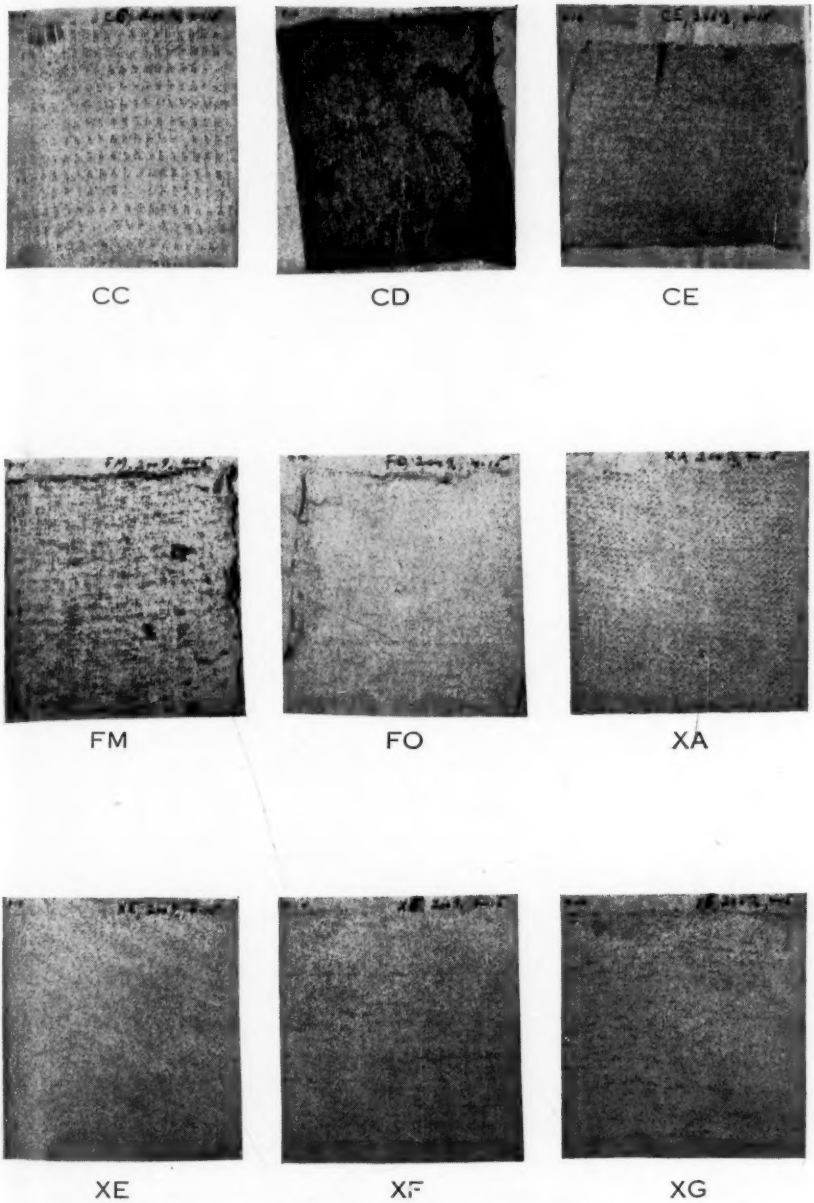


FIGURE 4.—*"Contact" impressions obtained with fabrics containing 200 percent of moisture.*

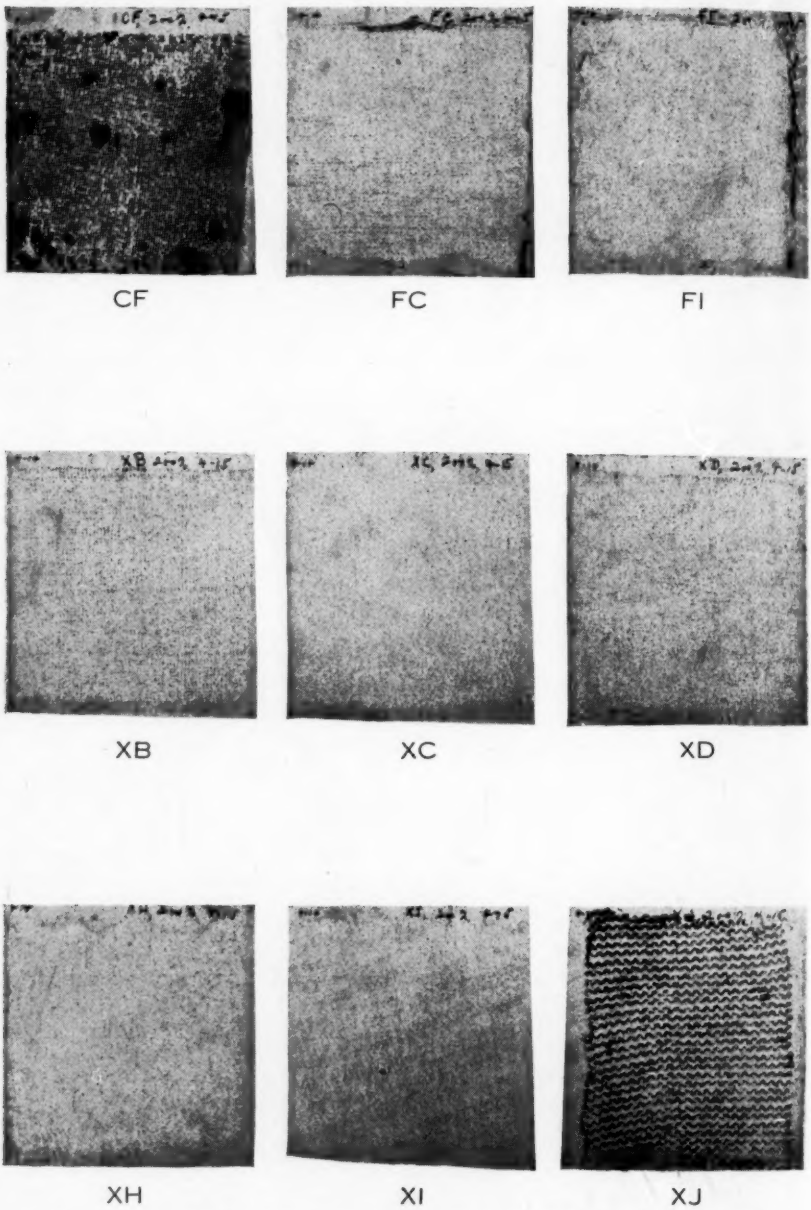


FIGURE 5.—*"Contact" impressions obtained with fabrics containing 200 percent of moisture.*

when the individuals perceived little or no difference in chilling effect, the sensitized papers showed that the two fabrics made similar contact. A typical series of contact papers, obtained when the fabrics contained 200 percent of moisture, is shown in figures 2 to 5. It is clear that, although all the fabrics contained equal percentages of water, some made better contact with the papers than others. Thus, for example, samples *A*, *G*, *M*, *FM*, amd *XJ* made very good contact, whereas others, such as *F*, *L*, *R*, *XC*, and *XI*, made poor contact. By increasing and decreasing the amounts of water in the fabrics their "tolerance" to moisture was estimated. It was found that even at 450 percent of moisture some of the fabrics (*L*, *CB*, *XE*, and *XH*) still did not completely color the papers. On the other hand, at 50 percent of moisture only fabrics *A*, *B*, *G*, *M*, *CF*, *FM*, and *XJ* colored the papers at all, and then only lightly. This variation in contact is shown graphically in figures 6 to 13, where the reflectance of the papers as measured photometrically is plotted against percentage of moisture in the fabrics.

To facilitate a more detailed discussion, the fabrics may be grouped according to weight, construction, and fiber composition.

TABLE 3.—*Subjective results obtained with fabrics containing 200 percent of moisture on the basis of their conditioned weights*

Samples compared	Subjective reaction	Samples compared	Subjective reaction
A and *F*	*A* much colder.	*F* and *XI*	*F* somewhat colder.
M and *O*	*M* much colder.	*CE* and *CF*	*CF* slightly colder.
N and *R*	Neither produces much chill, but *N* slightly colder.	*CE* and *CD*	Both cold, *CD* colder.
		XB and *XC*	*XB* cold, *XC* warm feel.
Q and *FO*	Neither causes much chilling, but *FO* slightly colder.	*FO* and *FI*	No difference.
G and *L*	*G* much colder.	*FM* and *FC*	*FM* colder.
		XJ and *XA*	Both cold, but *XJ* colder.
H and *K*	Both rather cool, *H* slightly cooler than *K*.	*CB* and *CA*	Very little difference, but *CA* may be slightly colder.
I and *FI*	*FI* slightly colder.	*CC* and *CD*	*CD* much colder.
A and *E*	*A* much colder.	*XE* and *XH*	Both comfortable, but *XE* very slightly colder.
B and *D*	*B* colder.		
C and *XD*	No difference noted.		
XF and *XG*	Both produce some chilling, but *XF* slightly colder.		

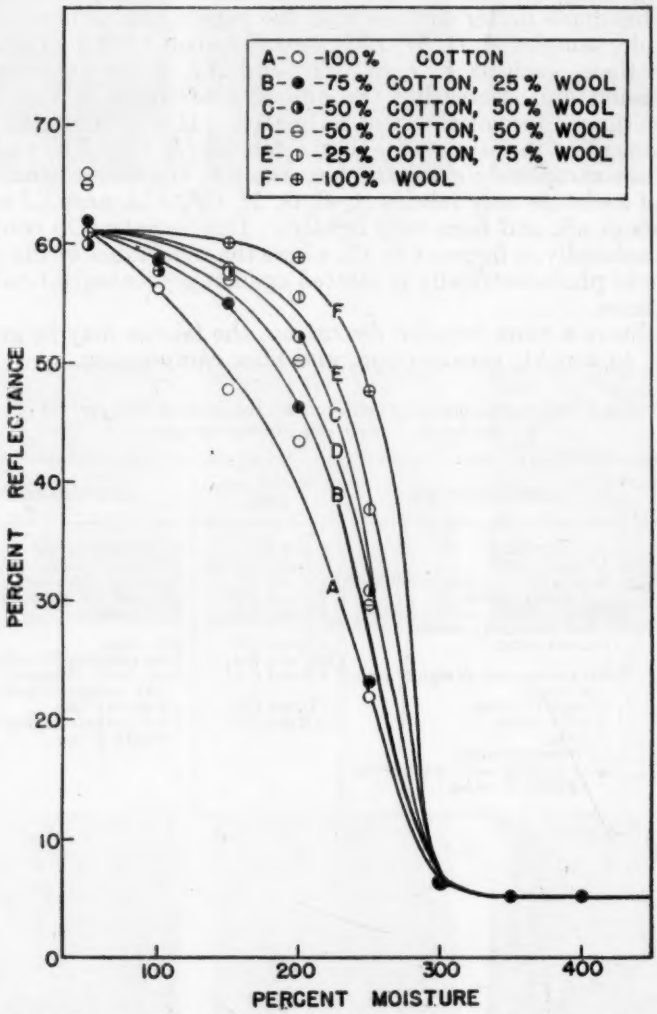


FIGURE 6.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

10½-lb fabrics composed of various percentages of cotton and wool.

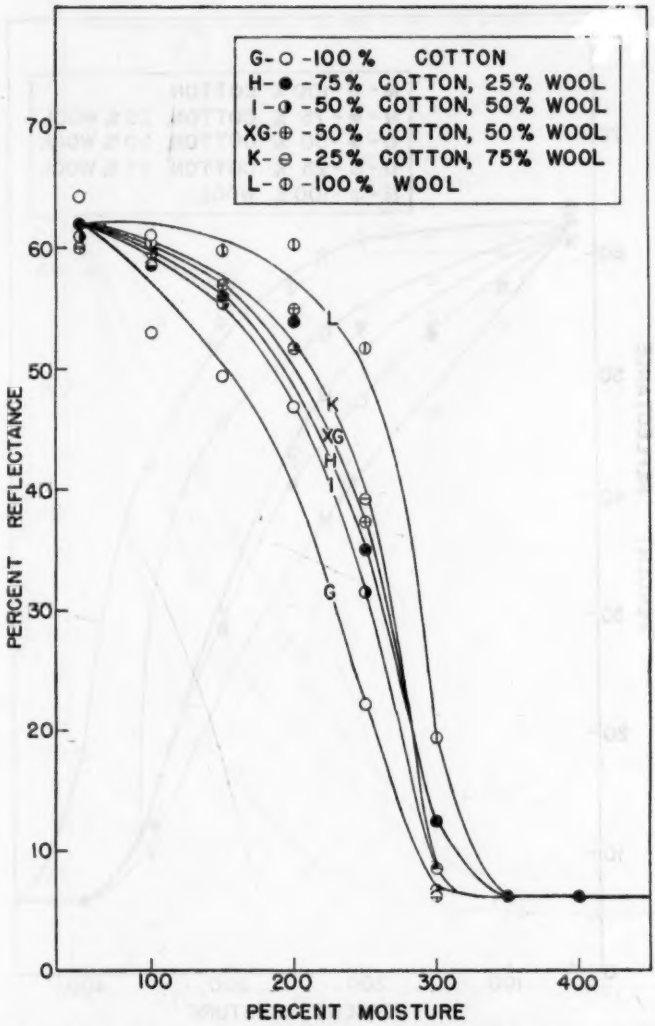


FIGURE 7.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

8- to 8¼-lb fabrics composed of various percentages of cotton and wool.

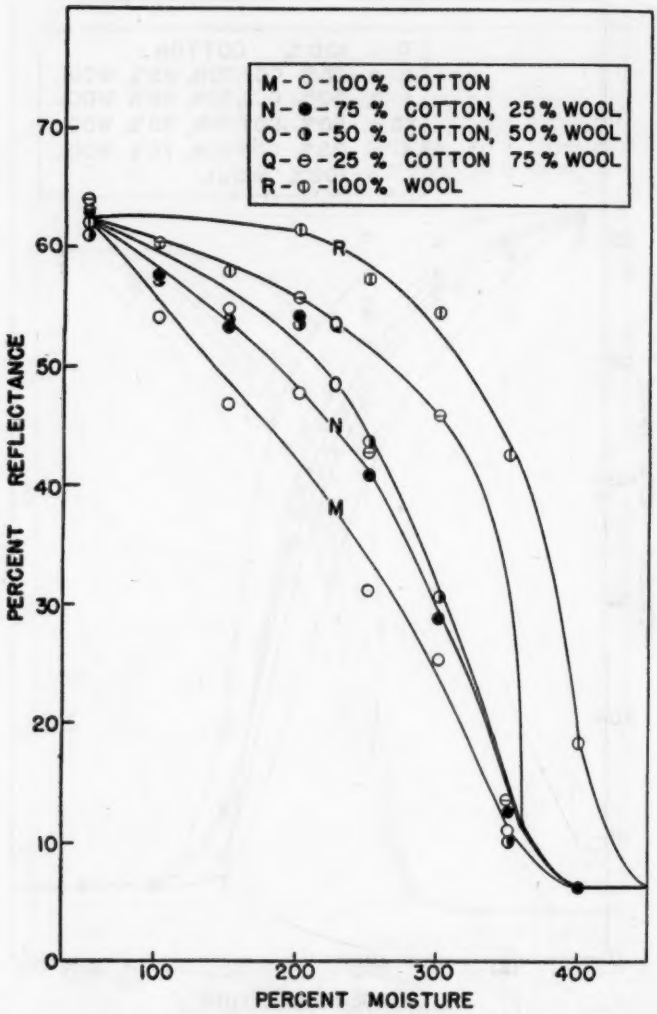


FIGURE 8.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

5½- to 6-lb fabrics composed of various percentages of cotton and wool.

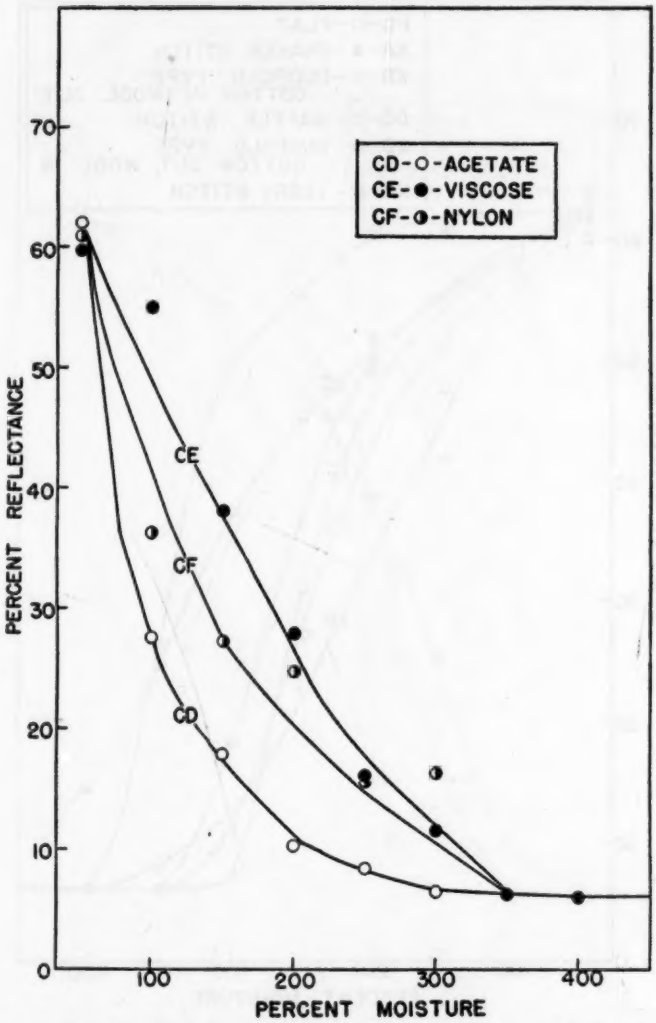


FIGURE 9.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

Lightweight fabrics made of continuous filament acetate, viscose, and nylon.

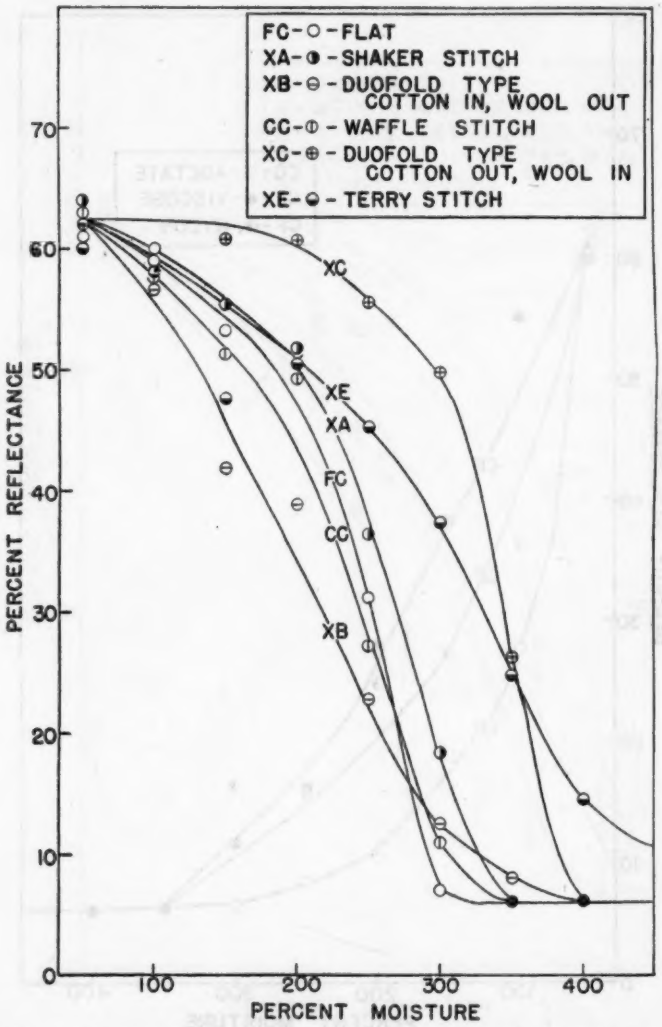


FIGURE 10.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

10½-lb fabrics of different constructions, composed of 50 percent of cotton and 50 percent of wool.

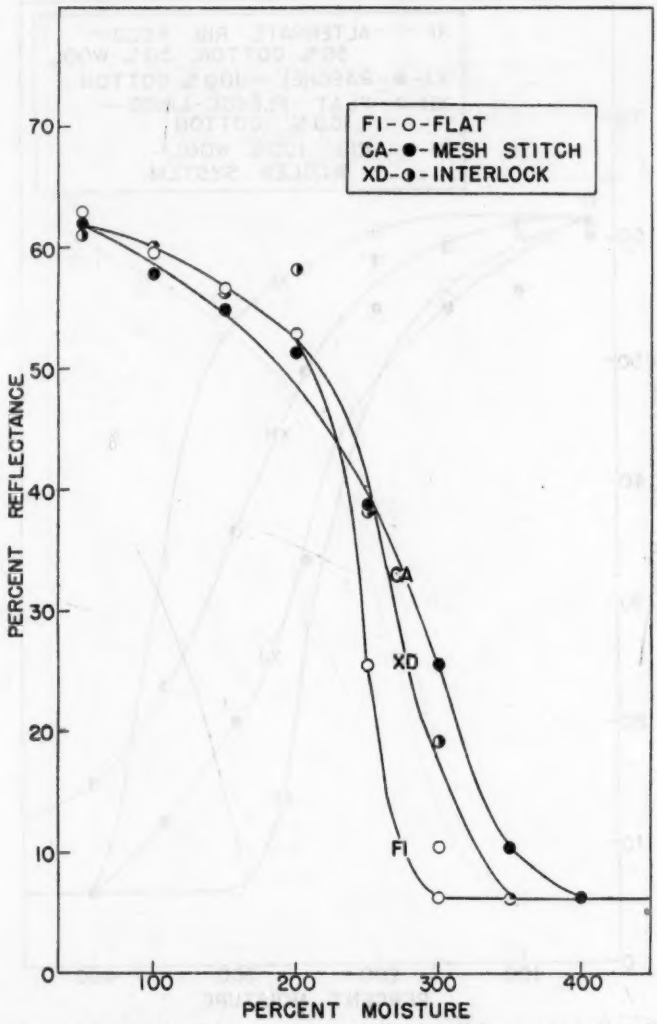


FIGURE 11.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

8- to 8¼-lb fabrics of different constructions, composed of 50 percent of cotton and 50 percent of wool.

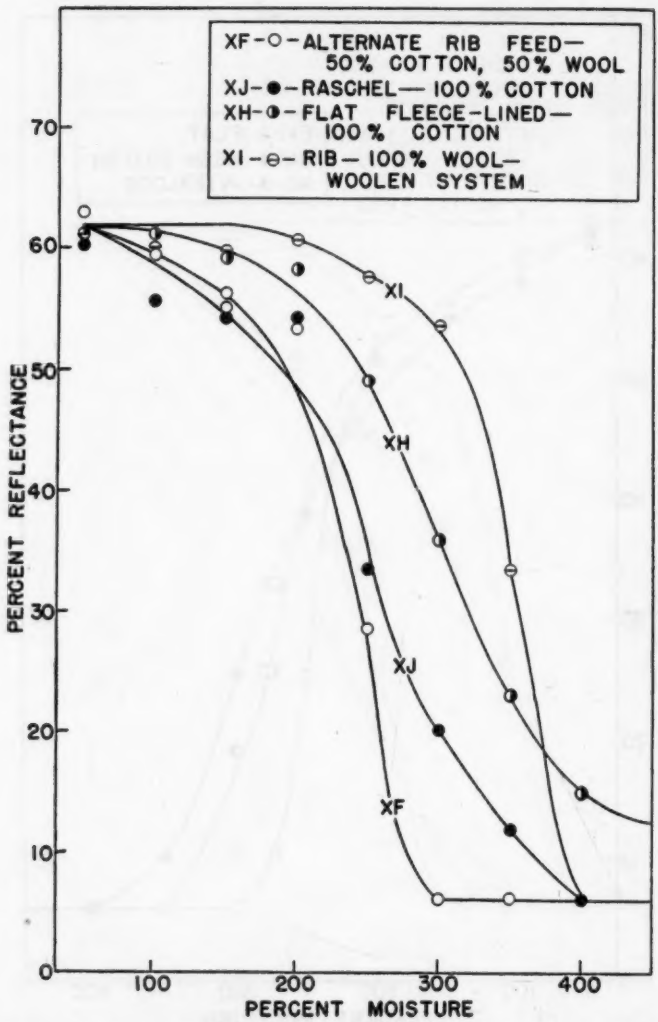


FIGURE 12.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

10½-lb fabrics of different constructions and various fiber compositions.

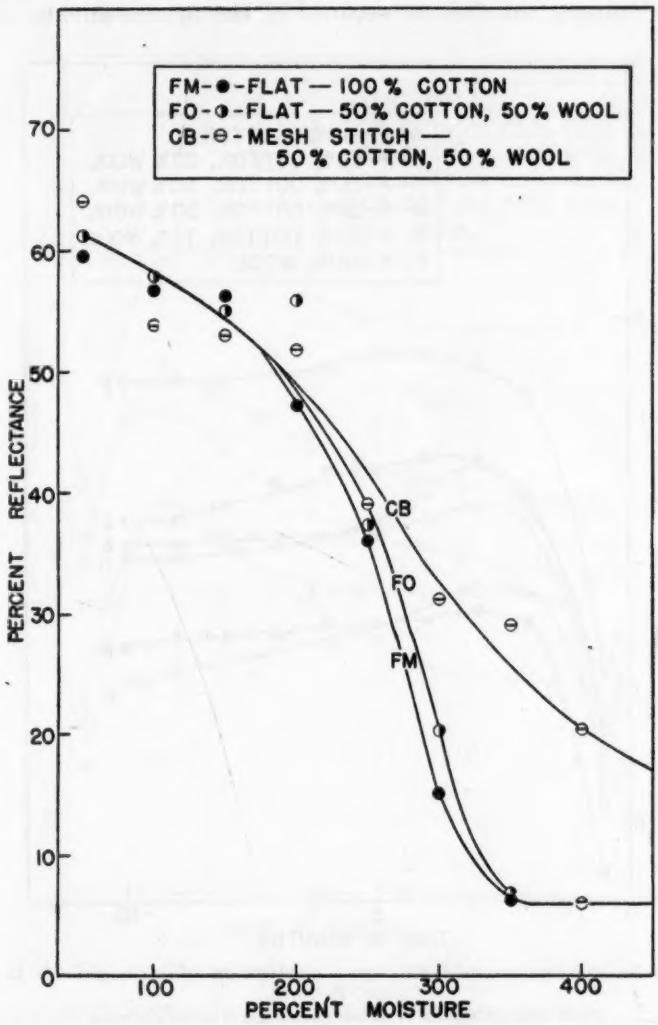


FIGURE 13.—*Reflectance of "contact" impressions obtained with fabrics containing various percentages of moisture.*

5½- to 6-lb fabrics of different constructions and various fiber compositions.

2. INFLUENCE OF FIBER CONTENT ON CHILLING EFFECT

Figures 14 to 17 show the drop in temperature caused by laundered fabrics of comparable weight and construction but of different fiber compositions. The curves show a rapid initial drop in surface temperature [7] during the first 30 seconds of the measurements, usually

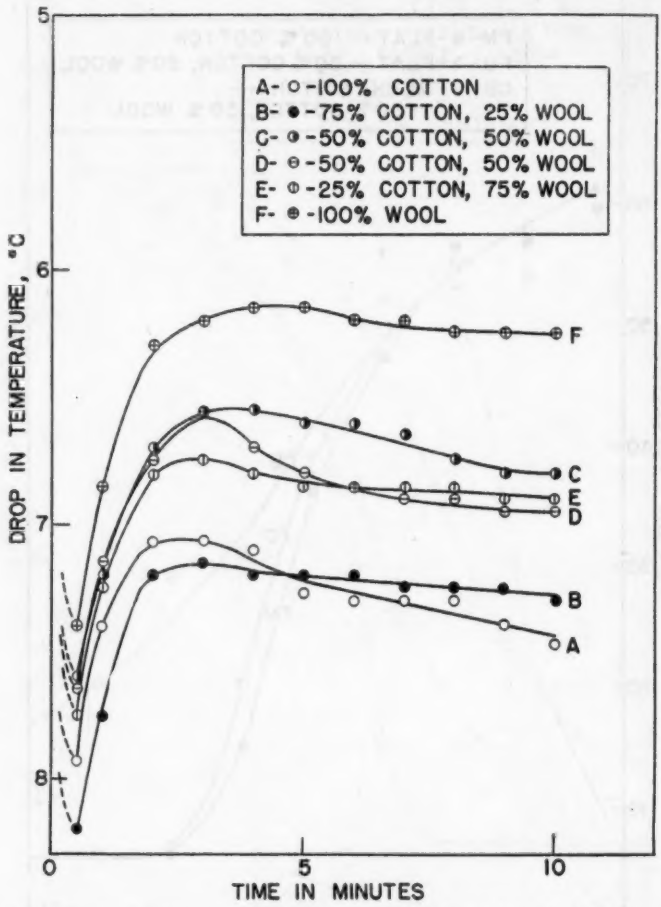


FIGURE 14.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

10½-lb fabrics composed of various percentages of cotton and wool.

followed by a slight increase in temperature, after which an approximately steady state is reached.

Since the thermocouple readings are influenced by the underside of the moist fabric as well as by the skin, the readings do not correspond precisely to the skin temperatures. This fact probably accounts in large measure for the unusual shape of the curves in the early portion

[7] In the course of measurements on the transmission of heat through textile fabrics, Rees [5] observed a very small drop in temperature when fabrics conditioned at 25° C and 65-percent relative humidity were brought in contact with a hot plate. The magnitude of the drop was greater for cotton than for woolen fabrics.

of the measurements. Thus, the rapid initial drop in temperature caused by the contact of the moist sample is followed by a rise in temperature, corresponding to an interval in which the heat supplied exceeds the heat lost by evaporation. When the loss of heat by evaporation becomes sufficiently great, a decrease in the thermocouple temperature again ensues. The heavier fabrics, because of their

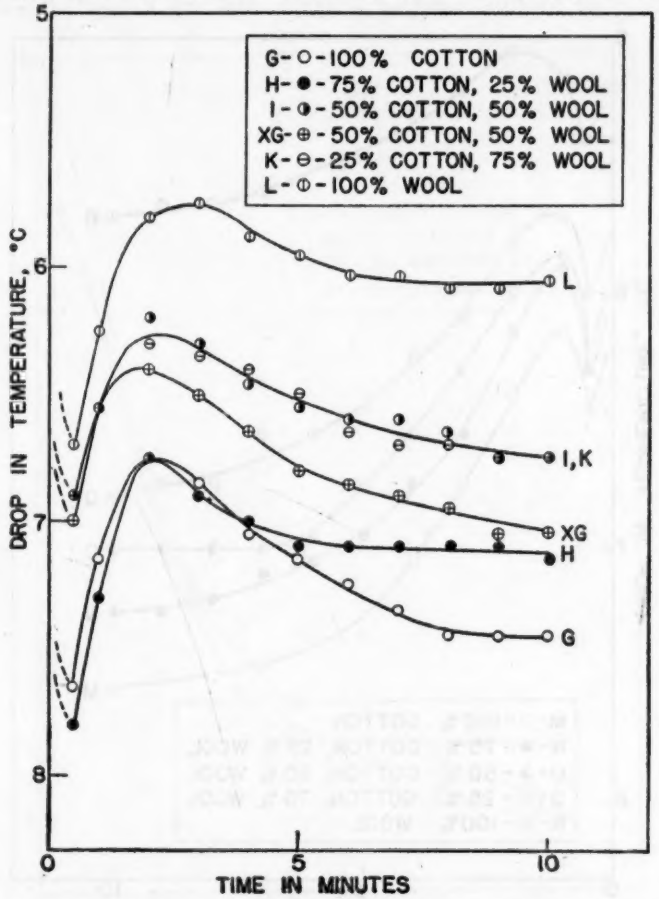


FIGURE 15.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

8 to 8¼-lb fabrics composed of various percentages of cotton and wool.

higher heat capacity and greater (absolute) content of water, cause a larger initial drop in skin temperature (compare figs. 14 to 17). On the other hand, a longer time is required for the evaporative losses to exceed the heat supplied in the case of the heavier samples.

In general, the results given in figure 14 show a regular, progressive decrease in the chilling effect of the 10½-lb [8] fabrics with increase in their wool content. Similar results for samples of nominal weights of 8 to 8¼ lb and 5½ to 6 lb are shown in figures 15 and 16, respectively. Sample *R* (fig. 16), which showed the smallest decrease in temperature

[8] The nominal weight of these fabrics is 10½ lb per dozen suits of size 40. For brevity, they will hereforth be designated "10½-lb fabrics," and a similar designation will be used for fabrics of other nominal weights. Although nominally the same, the fabrics differ appreciably in actual weight, as shown in table 1.

of all the rib-knit samples, was characterized by a very fuzzy surface after laundering and was considerably thicker than the other fabrics of comparable weight. Comparison of the curves showing a drop in surface temperature (figs. 14, 15, and 16) with those showing the reflectance [9] of the contact papers (figs. 6, 7, and 8) reveals a good qualitative relation between these two sets of measurements.

Figures 9 and 17 show the reflectance of the contact papers and the

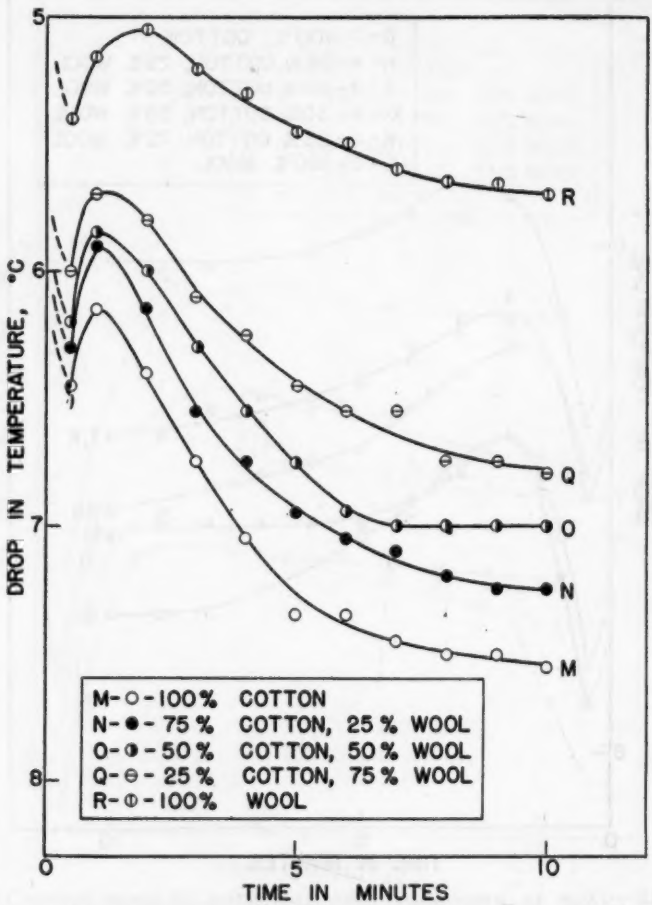


FIGURE 16.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

5½- to 6-lb fabrics composed of various percentages of cotton and wool.

drop in temperature, respectively, of the lightweight, continuous-filament underwear samples. These fabrics cause a big drop in temperature, but the differences between the acetate, viscose, and nylon fabrics are not large, and are of questionable significance. The diffi-

[9] The more color produced on the papers as a result of contact with the wet fabrics, the lower is their reflectance.

culty in manipulating these very thin fabrics in the various tests may account in part for the low correlation of the contact and temperature measurements.

3. INFLUENCE OF CONSTRUCTION ON CHILLING EFFECT

Figures 18 and 19 show curves of the drop in temperature obtained with fabrics of varied knit but of the same fiber content (50% cotton,

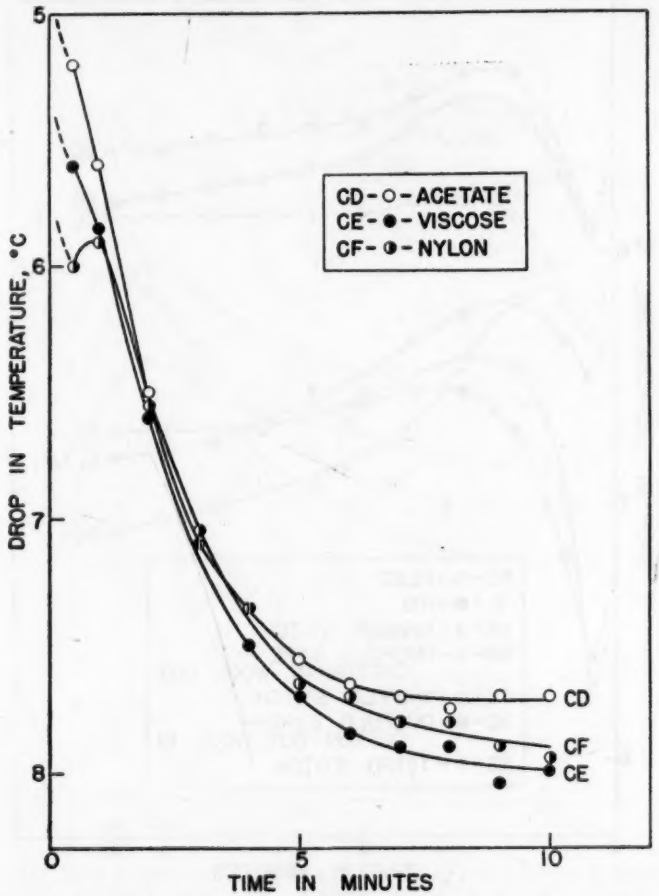


FIGURE 17.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

Lightweight fabrics made of continuous filament acetate, viscose, and nylon.

50% wool). The curves of rib-knit fabrics (samples *C* and *I*) are included for comparison. Because of the complexity introduced by fabrics of different constructions, the apparent relation between drop in temperature (figs. 18 and 19) and extent of contact (figs. 10 and 11) is not so close as with fabrics of simple rib knit. However, fabrics *XE* and *XC* (terry stitch and duofold[10] with wool inside, respectively)

[10] The duofold fabrics consist of two layers, one all cotton and the other all wool.

appear to be superior to the conventional rib knit. Since the duofold fabrics are identical, except that one has cotton and the other wool on the inside, a comparison of the results for these two samples clearly shows the advantage of having wool next to the skin rather than cotton. Although fabrics which are superior at one moisture percentage are usually superior at another also, this is not always the case, as is shown by crossing of the reflectance curves.

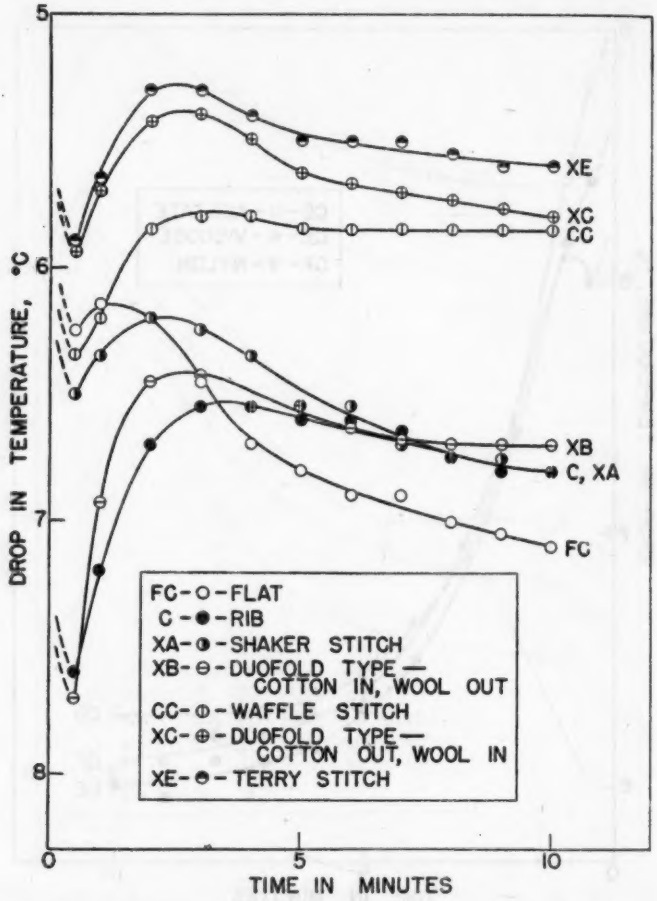


FIGURE 18.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

10¼-lb fabrics of different constructions, composed of 50 percent of cotton and 50 percent of wool.

Figures 20 and 21 show the drop in temperature for two groups of fabrics of various constructions and fiber compositions. Figures 12 and 13 indicate the contact made by the same fabrics. The results of the two sets of measurements show a good qualitative relation, the fabrics causing the least drop in temperature being the ones which make the poorest contact. Sample *XI*, which is an all-wool fabric spun on the woolen system, is among the best of all the fabrics tested.

The marked improvement that a fleece lining makes in an all-cotton fabric is illustrated by the curve for *XH*.

Throughout the investigation the moisture content of the samples was calculated on a percentage basis. If the fabrics had been tested with a given moisture content per unit area, the relative merits of the

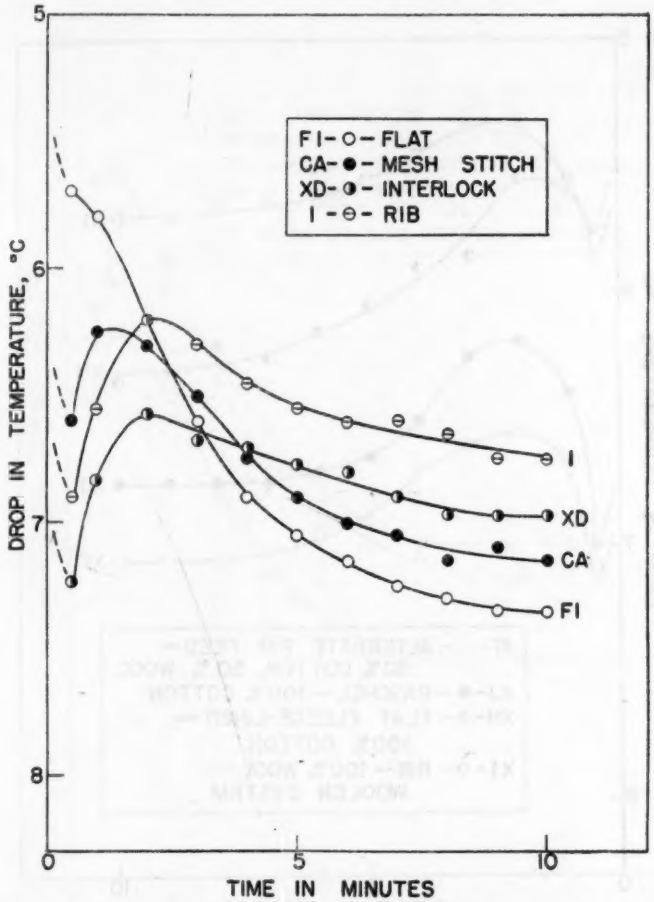


FIGURE 19.—*Drop in temperature upon application of moist fabrics to heated "skin" surface*

8- to 8¼-lb fabrics of different constructions, composed of 50 percent of cotton and 50 percent of wool.

various fabrics may have been somewhat changed. It is believed, however, that a similar basic relation between subjective tests, direct measurements of drop in temperature, and extent of contact, would still have been found.

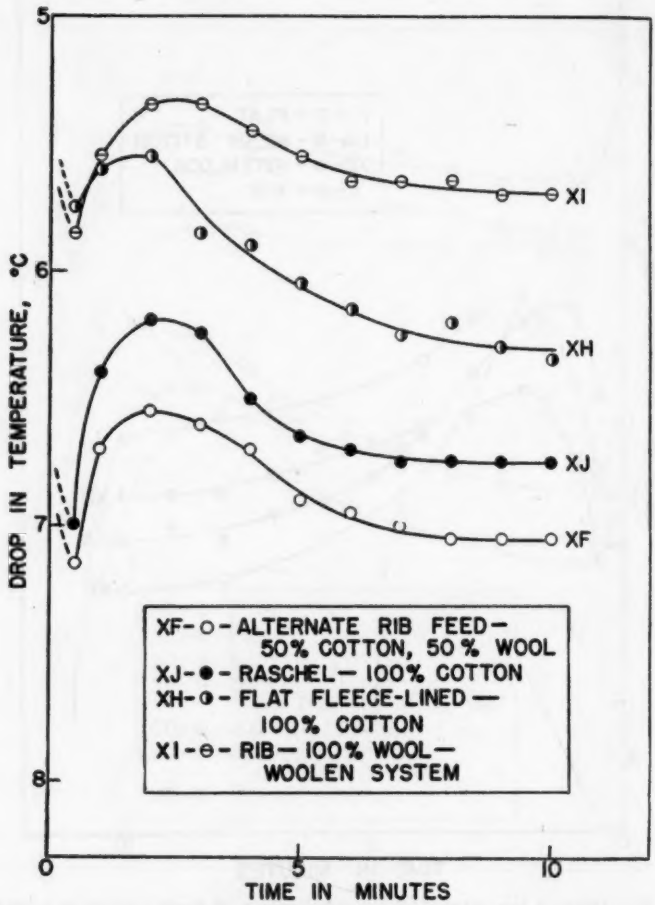


FIGURE 20.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

10½-lb fabrics of different constructions and various fiber compositions.

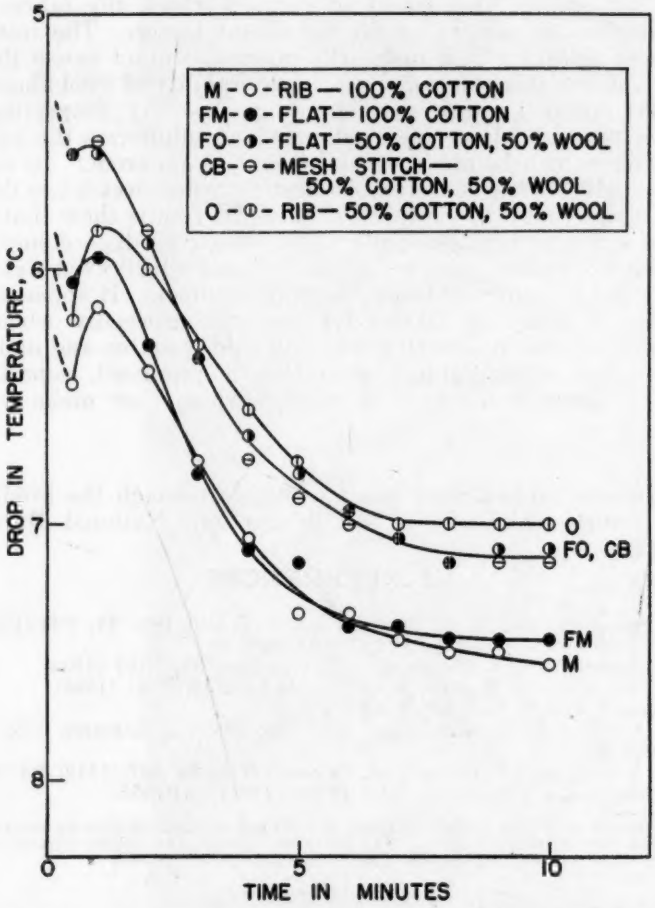


FIGURE 21.—*Drop in temperature upon application of moist fabrics to heated "skin" surface.*

5½- to 6-lb fabrics of different constructions and various fiber compositions.

V. CONCLUSION

Although it is difficult to rate on an absolute basis the "chilling effect" produced by the diverse fabrics which were included in these tests, several important conclusions can nevertheless be drawn—thus, a progressive improvement of the fabrics as their wool content is increased and the superiority of certain types of construction are clearly indicated. The extent of contact which the fabrics make with the skin appears to be the significant factor. The tests show that those fabrics which make the poorest contact cause the least chilling. From this point of view, the desirability of wool fibers which are highly crimped and possess long range elasticity, properties which permit a type of fabric construction which minimizes the extent of contact which can be made with the skin, is apparent. In contrast cotton which exhibits considerable plasticity when wet is less desirable from the same point of view. However, the results show that special types of construction, especially those which produce a napped, or fuzzy, surface reduce appreciably the contact which even wet cotton fabrics make and thereby lessen the chilling effect. It appears, therefore, that in selecting fabrics for warmth, especially when these fabrics are to be worn next to the skin in cold climates and under conditions where considerable perspiration is produced, consideration should be given to the type of contact which they make with the body.[11]

The data in table 2 were made available through the kindness of W. D. Appel, Chief of the Textile Section, National Bureau of Standards.

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[11] It is suggested that the type of contact may also be a factor in selecting fabrics for garments to be worn in hot climates, where keeping the body cool is a primary consideration. Preliminary evidence is available which indicates that for hot, humid regions, thin, flat fabrics are highly desirable.

WASHINGTON, January 4, 1944.